ONLINE MONITORING OF NITROGEN GREENHOUSE GASES FROM WATER RECLAMATION PLANTS

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DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously

WANG MENG

2 March 2015

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SUMMARY

Nitrous oxide (N_2O) has become a global concern as it is found to have global warming potential 310 times higher than carbon dioxide (CO_2) and has a longer lifespan in atmosphere. It has been reported that water reclamation plant (WRP) engaging biological nutrients removal (BNR) processes can significantly increase urban N_2O emissions, where N_2O is produced from both nitrification and denitrification stages as an intermediate. This implies that WRPs could be contributing to global warming considerably more than currently expected. Till now, only a few studies have been dedicated to this issue mostly due to the challenge of quantifying gaseous nitrogen greenhouse gas emissions from open or covered wastewater surfaces in treatment tanks in a WRP. As a response to the governmental concern of climate change, a study on online monitoring of N_2O emissions from Singapore WRPs has been conducted. A surface emission isolation flux chamber has been modified based on the USEPA standard method for the in-situ measurement of the surface emission of N_2O from full-scale BNR processes. This newly established prototype has been used for a group of real-time online monitoring at aerobic/anoxic BNR reactors in the past one and half year at two WRPs in Singapore – Changi Water Reclamation Plant (CWRP) and Ulu Pandan Water Reclamation Plant (UPWRP). Comprehensive 24-h N_2O emission profiles of BNR processes in both plants were obtained successfully. From the online monitoring data, N_2O emission fractions of incoming nitrogen loading were calculated to be 1.88±0.116% and 0.168±0.026% from CWRP and UPWRP, respectively. Meanwhile, corresponding mixed liquor characteristics including nitrite, nitrate and dissolved oxygen concentrations were analyzed.

Outstanding positive correlations have been observed between nitrite and N_2O emission. It has been found that there is potential for the CWRP to reduce the N_2O emission if its BNR process achieves full nitrification. The amount of N_2O emission from the full-scale WRP could be directly affected by the amount and quality of daily domestic wastewater generation and the operational conditions of the biological process. This study provided a sight of the N_2O emission baselines from the monitored WRPs, while it did not reflect the annual trend of N_2O emissions due to time limitation.

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ABBREVIATIONS

AOA	Ammonia-oxidizing archaea
AOB	Ammonia-oxidizing bacteria
BNR	Biological nutrients removal
BOD	Biological oxygen demand
CMD	Cubic meter per day
COD	Chemical oxygen demand
CWRP	Changi Water Reclamation Plant
DO	Dissolved oxygen
DTSS	Deep Tunnel Sewerage System
GC	Gas chromatograph
GHG	Greenhouse Gas
GWP	Global warming potential
NOB	Nitrite-oxidizing bacteria
PCC	Pearson Correlation Coefficient
SEIFC	Surface Emission Isolation Flux Chamber
SW	South Work
TKN	Total Kjeldahl nitrogen
UPWRP	Ulu Pandan Water Reclamation Plant
WRP	Water reclamation plant
WWTP	Wastewater treatment plant

Chapter 1: Introduction

1.1. Global Warming and Major Greenhouse Gases

Since the beginning of the 20th century, it has been observed that the average temperature of Earth's climate system, including air and sea, has been rising at a century scale. Studies in the past few decades indicated that human factors result in enhancing greenhouse effect and give rise to the global warming. With growing scientific understanding, the Intergovernmental Panel on the Climate Change (IPCC) has reported that in the past fifty years, the dominant cause of the observed global warming has been extremely likely to be the increasing concentration of anthropogenic greenhouse gases in the atmosphere (IPCC, 2007a).

It has been studied in recent period that the global warming effect caused by human activity like burning of fossil fuel and deforestation is higher than that which is caused by the change of solar radiation and volcanic activity (Hegerl et al., 2007). The significantly growing concentrations of greenhouse gases in the atmosphere since the pre-industrial times have drawn great attention. It has been listed in the Kyoto Protocol the foremost greenhouse gases under international concern, which include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and halocarbons. Report shows that in the 1750s, the concentration of CO_2, CH_4 and N_2O was about 280 ppmv, 700 ppbv and 275 ppbv, respectively (IPCC, 1995). The recent report shows that the concentrations of these greenhouse gases increased to around 398 ppmv, 1835 ppbv and 328 ppbv, respectively of CO_2, CH_4 and N_2O (NOAA, 2015).

The non-CO_2 greenhouse gases, primarily methane and nitrous oxide, have sustained a stable abundance in the atmosphere for the past few centuries even though they are largely emitted in the nature (IPCC, 2001). The major anthropogenic sources of these two non-CO_2 greenhouse gases include energy sectors, industrial processes, agriculture and waste management (UNFCCC, 1998). Nitrogen oxides (NO_x), in terms of the mixture of nitric oxide (NO) and nitrogen dioxide (NO_2), have been identified to be indirect greenhouse gases resulted from their reactivity (IPCC, 2001). Despite being not significant direct greenhouse gases, these reactive gases are able to affect the abundance of those direct greenhouse gases through atmospheric chemistry.

1.2. Nitrous Oxide – Role and Emission

The United Nations Framework Convention on Climate Change (UNFCCC) (2014) reported that the 100 years Global Warming Potentials (GWPs) of N_2O is 310, as compared to that of CO_2 and CH_4, which is 1 and 21, respectively. Besides high GWP, N_2O also has a long lifespan in the atmosphere of 120 years (UNFCCC, 2014). N_2O has been also recognized to be one of the most dominant ozone-depleting substance emitted in the 21st century (Ravishankara et al., 2009). The facts above show that N_2O emission into atmosphere has great impact on the global climate system that will last till the next century.

As a part of the Earth's nitrogen cycle, nitrous oxide is naturally present in the atmosphere with various natural resources. Since the pre-industrial era, N_2O emission has been increased by human activities such as agricultural soil

management, industrial chemical production, fossil fuel combustion, transportation and wastewater management. By statistics of the USEPA, around 40% of global N_2O emissions come from human activities (Anderson et al., 2010). It has been reported that till 2004 nitrous oxide had contributed 7.9% of anthropogenic greenhouse gas emissions to global radiative forcing (IPCC, 2007b).

1.3. Wastewater Treatment and N_2O Emissions

It has been reported that water reclamation plants, especially those having biological nutrient removal (BNR) processes, where N_2O is produced from both nitrification and denitrification stages as an intermediate, can significantly increase urban N_2O emissions (Townsend-Small et al., 2011). IPCC (2007b) reported that the nitrous oxide emissions from wastewater management account for almost 2.8% of the overall anthropogenic sources and rank as the sixth largest contributor. This figure implied that WRPs could be contributing to global warming considerably more than currently expected. Global N_2O emission from wastewater treatment processes is 0.22TgN/yr (Mosier et al., 1999). According to the IPCC (2001), the emission from wastewater treatment processes equals to 3.2% of total anthropogenic N_2O emission (6.9TgN/yr) and 1.3% of total N_2O emission (16.4TgN/yr). The N_2O emission from wastewater treatment sector contributes up to 26% of the total greenhouse (CO_2, CH_4 and N_2O) emissions, from the water chain including drinking water production,

water transportation, wastewater and sludge treatment and discharge (Frijns et al., 2008).

1.4. Singapore Water Reclamation Plants

1.4.1. Introduction of Singapore Wastewater Treatment Industry

The rapid growth of Singapore in the past few decades has led to an expansion of used water network. The development of modern wastewater infrastructure in Singapore satisfies a fast growing clean water demand. Nowadays, 100% of Singapore's population is served by its modern sanitation and sewerage system. Wastewater in Singapore is treated at three domestic water reclamation plants in the west, i.e., the Kranji WRP, Ulu Pandan WRP and Jurong WRP, and one centralized water reclamation plant in the east, i.e., the Changi WRP. The WRPs use biological process to remove the organic matters and nutrients in the wastewater. The treated water is discharged into the sea or alternatively it is further processed into NEWater. NEWater is the brand name of the produced ultra-clean water from reclaimed water through advanced membrane technology and ultraviolet disinfection.

Public Utilities Board, known as PUB, which is Singapore's national water and sanitation agency, carries out the application of comprehensive odor control facilities. All existing WRPs' treatment units were covered up with odor containment covers to minimize the odor nuisance caused to the surrounding environment. Extensive odorous air is delivered by air extraction systems to

odor treatment plants. The odorous air is treated through a treatment process with chemical scrubbing or activated carbon adsorption or both of them to remove hydrogen sulfide (H_2S) before discharging to the atmosphere. This action frees up more land for more valuable development with a reduced odor buffer zone.

1.4.2. Changi Water Reclamation Plant

The Changi Water Reclamation Plant (CWRP), opened in 2009, is Singapore's largest centralized water reclamation facility. CWRP is located at the easternmost of Singapore as a part of the first phase of deep tunnel sewerage system (DTSS). Besides CWRP, phase one of DTSS includes a 48km long underground tunnel from Kranji to Changi and 60km of link sewer, collecting half of Singapore's domestic and industrial wastewater. CWRP receives and treats a combination of domestic wastewater, infiltration and light industrial wastewater. The designed capacity of CWRP is 800,000 cubic meters per day (CMD) and is expected to have phased expansion until it reaches 2,000,000 cubic meters. The plant's treatment capacity has been expanded to 860,000 CMD.

Wastewater that enters CWRP is treated by solids and nutrients removal processes. After removal of debris, small particles, grit, oil, grease and heavier organic particles by preliminary and primary treatment processes, the wastewater is fed into bioreactors. Nutrients and colloidal organic matters are decomposed by microorganisms and the resultant used water enters secondary

sedimentation tanks for the bulky microorganisms to settle down. A portion of settled activated sludge is sent back to the bioreactors and the rest is sent for solids processing. The treated used water from secondary sedimentation tanks is either discharged through deep sea outfall pipes or transferred to a NEWater plant for further purification.

The odor control facilities in CWRP pump off-gas from all the biological reactors and clarifiers in the treatment modules to a centralized gas treatment system. The off-gas collected goes through activated carbon in the system, which targets to remove H_2S, followed by discharge to the atmosphere.

1.4.3. Ulu Pandan Water Reclamation Plant

The Ulu Pandan WRP is a municipal operated water reclamation plant located at the south-west of Singapore. The UPWRP was commissioned in 1961 with a total treatment capacity of 361,000 CMD. The extension of the plant was carried out by PUB using compact and covering design concept to save more land. The design concept includes compact construction of various treatment units and tanks using common walls and roof over the tanks with concrete slabs. The extension was completed in the end of the 1990s. Odor control facilities were installed at the same period.

The plant has two separate biological treatment processes, known as the South Work and North Work. The main processes involved in the South Work include a combined activated sludge and nutrient removal process. This process

achieves high treatment efficiency and the effluent quality is less affected by incoming loading fluctuations. All treatment modules are covered and the foul air is treated in a four-stage scrubber and activated carbon adsorption system.

1.5. Research Aims and Objectives

As a response to the government's concern of climate change, thorough monitoring of N_2O emission from WRPs has been conducted as the first attempt of this real time online monitoring in Singapore. This study targets to:

- Establish a prototype which is suitable for real time online monitoring of nitrogen greenhouse gas emissions from Singapore WRPs.
- Get the N_2O emission baselines from Singapore WRPs using the developed prototype based on the data from the real time online monitoring.
- Understand the correlations between wastewater characteristics and gaseous N_2O emission in a full-scale BNR plant.

1.6. Organization of the Dissertation

This thesis consists of six chapters. The first chapter has described the background of this work and introduced Singapore's existing water reclamation plants. The rest of this dissertation is organized as follows:

Chapter 2 reviews the existing literature relevant to BNR processes, dynamics of N_2O production from BNR processes, existing monitoring methods and results of N_2O emission from full-scale BNR processes, as well as the influencing factors that affect N_2O emission from BNR processes.

Chapter 3 describes the modification and improvements of the online gas sampling system. This chapter also presents the experimental and analytical methodology which has been used in the research.

Chapter 4 and chapter 5 provide the comprehensive online monitoring results of CWRP and UPWRP, respectively. These two chapters also discuss the overall N_2O emissions from the BNR processes, the corresponding emission fractions, the correlations between N_2O emission and wastewater characteristics and N_2O emission monitored at the odor control system.

Chapter 6 presents conclusions of this research and relevant recommendations.

Chapter 2: Literature Review

2.1. Biological Nitrogen Removal Processes and N_2O Emission

Nitrogen in raw wastewater is present in the form of organic nitrogen, ammonium (NH_4^+) and very low concentrations of nitrite (NO_2^-) and nitrate (NO_3^-). The complex organic nitrogen compounds such as amino acids, amino sugars and proteins are usually readily converted to ammonium by biodegradation in the sewage system and in the bioreactors (Metcalf and Eddy, 2003). In a conventional BNR process, NH_4^+ is converted to NO_2^- and then NO_3^- through autotrophic nitrification, after which the NO_3^- and residual NO_2^- are reduced to N_2 via heterotrophic denitrification. Nitrification process requires adequate aerobic conditions, whereas denitrification process needs anoxic conditions where sufficient external organic carbon resource is provided. The BNR systems are engineered to provide compatible conditions to enable both nitrification and denitrification process to operate efficiently.

N_2O is well known as an obligatory intermediate in the heterotrophic denitrification pathway during the biological nutrient removal processes. It is also produced by autotrophic nitrifying bacteria during nitrification process as a by-product (Kampschreur et al., 2008). Among the nitrogen oxides, nitric oxide (NO) is a precursor in the N_2O formation, and is formed in both nitrification and denitrification processes (Chandran, 2012). Nitrogen dioxide (NO_2) is formed by the chemical oxidation of NO.

2.2. Dynamics of N_2O Production

2.2.1. N_2O Produced by Autotrophic AOB

In the nitrification process, ammonia is consumed by autotrophic ammonia-oxidizing bacteria (AOB) or ammonia-oxidizing archaea (AOA) and converted to nitrite, followed by further conversion to nitrate through metabolism of nitrite-oxidizing bacteria (NOB).

The reduction of NO_2^- to NO, N_2O and N_2 by autotrophic AOB is known as nitrifier denitrification. It has been found from previous studies that only genes encoding NO_2^- and NO reductase but not N_2O reductase were found in the genome of AOB (Cantera and Stein, 2007; Casciotti and Ward, 2005; Garbeva et al., 2007; Shaw et al., 2006), which indicate that N_2O is the potential end product of the process but not N_2 for the AOB. Nitrifier denitrification of AOB plays the key role of N_2O generation in autotrophic nitrification especially under oxygen-limiting or anoxic conditions (Goreau et al., 1980; Hooper et al., 1997; Kampschreur et al., 2008a, 2008b; Schmidt and Bock, 1997), whereas NOB does not contribute to N_2O production. More studies showed that denitrification activity of AOB is the predominant source under nitrifying condition in the activated sludge process (Kim et al., 2010), and can contribute more than 80% of the N_2O emissions depending on dissolved oxygen (DO) level (G Tallec et al., 2006).

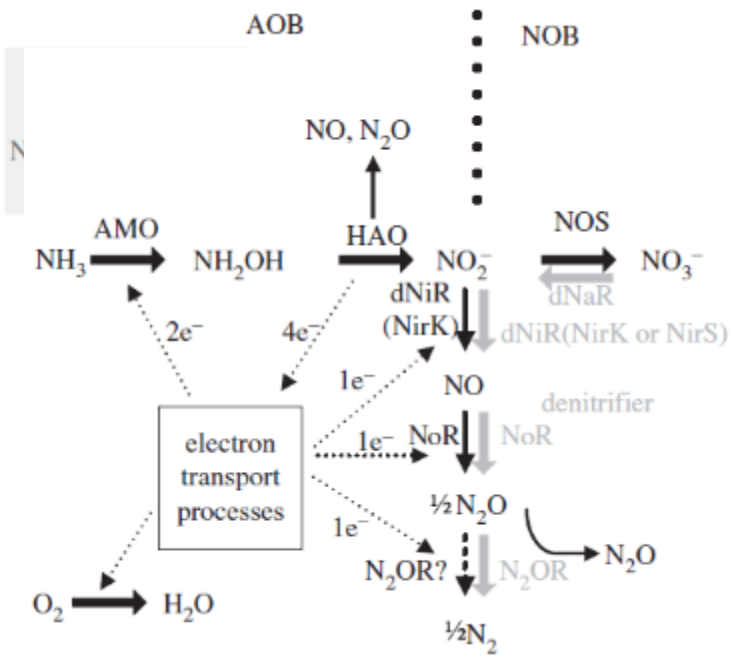


Figure 2.1. Nitrogen transformation pathways of AOB, NOB and denitrifying bacteria (source from Kim et al., 2010; modified by Law et al., 2012). AOB and NOB pathways are divided by the thick dotted line and denitrifying pathway is shown in grey arrows.

Autotrophic ammonia oxidation is another pathway of N_2O production at nitrification stage (Figure 2.1). Ammonia (NH_3) in the wastewater is firstly converted by AOB to Hydroxylamine (NH_2OH) by ammonia mono-oxygenase (AMO). Subsequently, the produced NH_2OH as an electron donor is converted to NO_2^- by hydroxylamine oxidoreductase (HAO) (Andersson and Hooper, 1983). This NH_2OH oxidation step further involves two reactions that include conversion of NH_2OH to nitrosyl radical (NOH) and conversion of NOH to NO_2^-, which take place concurrently (Igarashi et al., 1997; Poughon et al., 2001). N_2O can be formed through the decomposition of the unstable NOH during the reactions (Poughon et al., 2001). However, the contribution of the N_2O production from this pathway in wastewater treatment needs further

confirmation. In addition to the breakdown of unstable NOH, biological reduction of NO produced during the oxidation of NH_2OH could also be a potential source of N_2O (Law et al., 2012).

2.2.2. N_2O Produced by Heterotrophic Bacteria

It has been proven that N_2O is produced during the sequential actions of the dissimilatory reduction of ionic nitrogen oxides during heterotrophic denitrification (Knowles, 1982). Nevertheless, it has been estimated that the maximum N_2O reduction rate could be four times faster than NO_3^- and NO_2^- reduction rates (Wicht, 1996). This estimation implies that in ideal situation, N_2O is not likely to accumulate in the wastewater during denitrification. However, in a full-scale plant the fluctuating environment will always cause inhibition of the N_2O reductase and lead to transient N_2O accumulations (Law et al., 2012). Additionally, N_2O has been found to be the end product of some denitrifiers as there is not much energy loss even if N_2O is not further reduced to N_2 (Brettar and Hofle, 1993; Richardson et al., 2009).

The transient accumulation of N_2O does not contribute to significant emission due to the lack of stripping by aeration in the anoxic zone. However, when the residual dissolved N_2O is carried over to the aeration zone, it will be stripped from liquid phase by the aeration (Ahn et al., 2010; Kampschreur et al., 2009).

2.3. N_2O Emissions from Full-Scale WRPs

Current method of estimation of N_2O emission from a wastewater treatment plant (WWTP) used by IPCC is based on an emission factor of 3.2 gN_2O/person/year from non-BNR processes and 7 gN_2O/person/year from BNR processes (Thomsen and Lyck, 2005). The factor is based on the earliest study conducted by Czepiel et al. (1995) in the US in an activated sludge plant. However, these factors may not be broadly representative because they are based on a set of limited data (Ahn et al., 2010; Ye et al., 2014).

Recent studies suggest that the majority of N_2O emission from BNR processes has been found to occur in the aeration zones (Ahn et al., 2010; Foley et al., 2010). Even though N_2O is an obligatory intermediate in the denitrification pathway, its formation in the anoxic zone would largely remain dissolved in the liquid phase. Most of the dissolved N_2O would be reduced to N_2 before it is transferred to the gaseous phase in anoxic zones. In contrast, the intensive aeration in the aerobic zone enables the quick transfer of newly produced N_2O from liquid phase to the gaseous phase (Ahn et al., 2010). The accumulated N_2O from the anoxic zone under temporary imbalance between production and consumption could also be stripped from the liquid phase when it enters the aerobic zone. In other words, the N_2O emitted with air stripping from the aerobic zone could be from both denitrification and nitrification. N_2O production may also occur in the anaerobic zone, primary sedimentation tanks and secondary sedimentation tanks, but at smaller amounts compared to that produced in the anoxic and aerobic zones (Foley et al., 2010). The emission of NO during the

processes are usually hundreds times lower compared to the N_2O emission, and the emission of NO_2 is even negligible (Chandran, 2012).

2.4. Sampling Strategies for Monitoring of N_2O Emission from Wastewater Treatment Plants

A closed floating chamber is always utilized for N_2O monitoring at full-scale wastewater treatment plants. The floating chamber technique is adapted from measurements of surface emission from soil. According to the USEPA online surface monitoring method and the California SCAQMD rule 1133 for measurement of gas emission from water surface, a surface emission isolation flux chamber (SEIFC) is commonly used for in-situ measurement (Chandran, 2010). The off-gas emits into the headspace of the floating chamber during aeration; during non-aerated stages, sweep gas is engaged to the chamber headspace to blow the off-gas out. For quantifying the surface emission flow rate, a tracer gas with known flow rate, usually chosen as an inert gas such as helium or argon, is introduced into the chamber headspace. The surface emission flow rate of off-gas is calculated from the dilution rate of the tracer gas.

The first report of measurement of N_2O emission from the wastewater treatment plant using a floating chamber was published by Czepiel et al. (1995) in the US. At that time, grab sampling was the main strategy when online monitoring had not been developed. The analysis of N_2O concentration in the off-gas was achieved by a gas chromatograph (GC). A similar study was conducted in Japan

through air pump and air sampling bags (Kimochi et al., 1998). It has been indicated that even though the floating chamber can capture the emitted N_2O, the off-line data from grab samples is unable to show the dynamic changes in the N_2O emission profile (Daelman et al., 2013a; Law et al., 2012), which could result in over- or under-estimation of the overall N_2O emission. In recent years, continuous online monitoring is employed to attain more accurate quantification of N_2O emission. For long-term monitoring, sampling during night-time and weekends would significantly contribute to the accuracy of the estimation (Daelman et al., 2013a). The type of online sensors used in various studies include infrared analyzer (Ahn et al., 2010; Butler et al., 2009; Daelman et al., 2013), chemiluminescence (Kampschreur et al., 2008a) and mass spectrometry (Otte et al., 1996; Zeng et al., 2003).

Other than temporal changes, spatial variation should also be taken into consideration during the online monitoring of the N_2O emission profile especially for continuous processes. Usually the online monitoring is carried out at different locations within one process, either by using multiple floating hoods at all locations simultaneously or by moving a single hood between different locations (Law et al., 2012).

Measurement of liquid-phase N_2O is primarily used for understanding the dynamics of N_2O production and emission rather than for quantification of N_2O emission (Law et al., 2012). The dissolved N_2O is usually measured by GC analysis of the off-line grab samples from wastewater, where it has been used for both laboratory-scale reactors and full-scale plants (Czepiel et al., 1995; Garrido et al., 1998; Kampschreur et al., 2008; Yang et al., 2009). Recent

studies engaged a N_2O micro-sensor, which is a modified Clark electrode and gives more sensitive and accurate results (Foley et al., 2010; Kampschreur et al., 2008).

2.5. Preliminary Study Conducted by PUB

PUB has conducted a preliminary study on estimation of N_2O emission from Singapore WRPs by using the IPCC emission factor and grab samples from the odor control system from 8am to 5pm during weekdays in 2010. It showed a great discrepancy in the N_2O emission amount resulted from the two methods, where the results from the grab samples were much greater than those calculated using the emission factor. The discrepancy implied the limitation of the empirical emission factor. Additionally, as the covered reactors in the Singapore WRPs are not perfectly isolated, the indirect online monitoring from air duct instead of wastewater surface may result in underestimation. Furthermore, the missing period of measurement, including night time and weekends, may also lead to inaccuracy of the emission results.

2.6. Limitations of the Existing USEPA Sampling Method

According to the USEPA standard online monitoring method and the California SCAQMD rule 1133, a surface emission isolation flux chamber (SEIFC) is commonly used for in-situ measurement utilizing a helium tracer gas. However, several drawbacks were found during previous applications in the measurement

of advective gas emission by using such method. Firstly, the standard 1/4' Teflon tubing will create a small resistance when transporting the gas out from the SEIFC. Back pressure generated in the narrow long tubing caused by the resistance would result in inaccuracy measurement (i.e., lower measured results) and a rise in internal pressure, which can also be affected by temperature and humidity. Meanwhile, it has been reported that the helium tracer gas method may also result in measurement deviation due to insufficient mixing of tracer gas in the floating chamber (Schmidt, 2008). This may cause major analytical error in back calculations of surface emission rate and concentrations of gaseous nitrogen compounds. It has also been found that simultaneous measurement of surface emission rate and gas concentrations in outlet samples for online monitoring is not reliable by using such SEIFC monitoring method.

2.7. Full-Scale N_2O Emission Data Obtained in Other Countries

Typically the N_2O emission rate is represented by an emission fraction defined by the ratio between the amount of emitted N_2O-N and the mass of total Kjeldahl nitrogen (TKN) in the influent. Alternatively, in some cases the emission fraction is represented by the ratio between the amount of emitted N_2O-N and the mass of total nitrogen removed through the BNR process (Law et al., 2012).

So far, only a few studies have been dedicated to the online monitoring of N_2O in WRPs, mostly due to the challenges of quantifying gaseous nitrogen greenhouse gas (GHG) emissions from open or covered wastewater surface in

treatment tanks. Of these studies at full-scale BNR processes, the N_2O emissions fraction reported vary substantially from 0 to 25% (Table 2.1). Most of the studies showed that the N_2O emissions were at a low percentage that within the range of 0~3%. However, it could be noticed that the studies on multiple plants of Wicht and Beier in 1995 and of Foley et al. in 2010 showed significantly high values in the range of N_2O emissions while the average emissions were as low as the other studies. This was explained by Foley (2010) that some WWTPs might operate steadily with relatively low N_2O emission, while when they were suffering some process perturbation, it may lead to a temporary spike in N_2O formation. This was witnessed at the two studies which had the peak N_2O emissions.

It should be noted that even 1% of increase in the emission fraction would lead to significant increase of the carbon footprint due to the huge base amount. The emission fraction varies from WWTPs and it is not recommended to extrapolate the plant emission of N_2O using empirical emission coefficients. The large variation of N_2O emission in different plants may be owing to diverse BNR process configurations and operational conditions, as well as different wastewater characteristics. Additionally, different monitoring strategies could be another contributing factor (Law et al., 2012).

Table 2.1. N_2O emission (% of influent N) reported for full-scale WWTPs.

Type of BNR process	*Sampling strategy*	*N_2O emission fraction (% of influent N)*	*Reference*
Activated sludge	Grab samples weekly for 15 weeks	0.035%	Czepiel et al., 1995
25 Activated sludge plants	Single grab samples per plant	0-14.6% (0.6% average)	Wicht and Beier, 1995
Activated sludge	Grab samples every alternative week for 1 year	0.001%	Sümer et al., 1995
Anoxic-aerobic activated sludge	Grab samples	0.001-0.04%	Benckiser et al., 1996
Activated sludge	Grab samples every 1 or 2 weeks over 1.5 years	0.02%	Sommer et al., 1998
Activated sludge	Online measurement for 2 hours	0.01-0.08%	Kimochi et al., 1998
Nitritation-anammox process	Online measurement for 4 days	2.3%	Kampschreur et al., 2008b
Partial nitritation-anammox sequencing batch reactor	Online measurement	0.4-0.6%	Joss et al., 2009
7 BNR plants	Grab samples	0.6-25.3% (3.5±2.7% average)	Foley et al., 2010
12 BNR plants	Online measurement	0.01-1.8%	Ahn et al., 2010
4 plants with different processes (completely mixed, plug flow, membrane	Online measurement	0-0.3%	Foley et al., 2011
Activated sludge	Online measurement	2.8%	Daelman et al., 2013

2.8. Factors Influencing N_2O Emission

Numerous factors have been found to be correlated to N_2O generation and emission during nitrification and denitrification stages from previous studies.

Operational conditions of a WWTP such as aeration will affect the N_2O emission directly to a greater extent in comparison with the emission from freshwater, ocean or soil. N_2O represents relatively higher solubility in water compared with oxygen (Law et al., 2012). This higher solubility implies that N_2O could accumulate in water to relatively high levels without presence of air stripping. This finding has been further proven by the study of Law et al. (2011), which reported that negligible amount of N_2O was observed to emit from a non-aerated nitrifying reactor, whereas the dissolved N_2O was promptly stripped out with the addition of aeration.

DO concentration is an important factor affecting N_2O emission in nitrification stage. There are contradictory observations from different studies. According to the study of Ahn et al.(2010), N_2O emission is positively related to DO concentration. However, Kampschreur et al. (2008b) reported that N_2O emission increased with decreasing DO concentration. Furthermore, transient changes in DO concentrations could cause prompt increase of N_2O emission, which usually happen during the transition between anoxic and aerobic zones especially for AOB (Kampschreur et al., 2008a; Kester et al., 1997; Yu et al., 2010).

Several recent studies have showed increasing concentration of NO_2^- would lead to larger amount of N_2O production by the AOB in full-scale WWTPs; studies

also reported observable correlation between N_2O production and high NO_2^- concentration (Chandran, 2012; Foley et al., 2010; Kampschreur et al., 2009, 2008b; Sümer et al., 1995). These findings have been further verified in laboratory-scale studies, in which NO_2^- accumulation can pulse N_2O generation through AOB (Kampschreur et al., 2008a; Tallec et al., 2006). Some recent studies dedicated to N_2O emission from partial nitrification (also known as nitritation) process showed that the amount of N_2O emission from partial nitrifying reactor may be up to 1.5 to 2.2 times higher than that from full nitrification process (Ahn et al., 2011; Rodriguez-Caballero et al., 2013; Wei et al., 2014). This may account for the accumulated NO_2^- during partial nitrification/nitritation process.

The availability and type of carbon source, which is expressed by chemical oxygen demand (COD), in denitrification stage is an important factor influencing the N_2O emission from denitrification (Chiu and Chung, 2000; Schalk-Otte et al., 2000). The COD/N ratio plays a key role in the completion of denitrification activity (Hanaki et al., 1992).

Temperature is an indirect factor that affects N_2O emission. The solubility of N_2O in water decreases with increasing temperature (Weiss and Price, 1980). This may lead to additional emission of N_2O from water when temperature increases. The solubility of N_2O in water is 1059.96 mg/L at ambient partial pressure of 1 and salinity of 0. The solubility of oxygen at the same condition is 8.12 mg/L. Other factors affecting N_2O emission from BNR process include rapidly changing process conditions such as ammonia shock loads (Burgess et

al., 2002), changes in nitrite concentration (Tallec et al., 2006) and indirect factors causing these changes (Kampschreur et al., 2009).

It was indicated in a recent study in Australia that WWTPs achieving near-complete denitrification (i.e. low TN in the effluent) would contribute to less N_2O emission compared to those with partial denitrification (i.e. higher TN in the effluent) (Foley et al., 2010). The designed features of the plants achieving low TN in the effluent, such as high activated sludge recycle rate, large bioreactor volume, long SRT and dosage of external carbon source, could probably lead to low N_2O generations. High activated sludge recycle rates tend to substantially dilute the concentrations of the intermediates during nitrification and denitrification, thereby reducing their inhibitory effect in N_2O formation. Larger reactors together with sufficient aeration capacity and a rapidly responding DO control system could help reduce the risk of the transient spikes of nitrite that are postulated to provide a precursor for N_2O formation (Foley et al., 2010).

2.9. Summary of the Research Aims

Due to the limitation of the existing USEPA floating chamber method, which is explained in section 2.5, there is a need to develop a better floating chamber and an improved prototype to achieve more accurate real time online monitoring of nitrogen greenhouse gas emissions from full-scale WRPs.

The N_2O emission from a WRP is highly dependent on the treatment process, wastewater quality and operational parameters. The influencing factors mentioned in the earlier section may not be the prerequisite conditions to determine the N_2O emission level of a WRP. Therefore, thorough monitoring of N_2O emissions from the BNR processes is required for Singapore WRPs in order to know the nation's N_2O emission baselines.

Based on the data from the real-time online monitoring using the developed prototype, it is able to understand the correlations between wastewater characteristics and gaseous N_2O emission in a full-scale BNR plant. This understanding will provide a practical basis for the future control of N_2O emission from Singapore WRPs.

Chapter 3: Prototype and Methodology

3.1. System Design

3.1.1. Assembling of Gas Analysis System

The concentration of nitrogen greenhouse gas in the exhaust gas is highly dynamic and can vary in a wide range. An N_2O analyzer (*ThermoScientific, model 46i-HL*) is used for analysis of N_2O concentration in gas samples. The N_2O analyzer has a detectable range of 0-2000 ppm and the lowest detectable limit of 0.3 ppm. The sample flow rate of the N_2O analyzer is 0.5 – 2 liters/min.

Another NO_x analyzer (*ThermoScientific, model 42i*) is used to measure the NO_x concentration in the gas samples that gives readings for NO, NO_2 and NO_x. The detectable range of NO_x concentration is 0-100 ppm and the lowest detectable limit is 0.4 ppb. The sample flow rate of the NO_x analyzer is around 0.6 liters/min.

A digital data logger record receives signal from both analyzers and records readings including N_2O and NO_x concentrations as well as the gas flow rates of both analyzers. The readings are recorded at an interval of 1 min.

3.1.2. Modification of Surface Emission Isolation Flux Chamber

The newly modified SEIFC prototype developed in this study is based on the USEPA standard method but without the usage of helium tracer gas. Instead, a

gaseous flux sensor, *Velocicalc Multi-Function Ventilation Meter Model 9565 (TSI, USA)*, was introduced by modifying the SEIFC as shown in Figure 3.1. Online N_2O, NO and NO_2 analyzers were connected to the SEIFC by 1/4' Teflon tubing with a stable suction of gas samples from the modified SEIFC. An open chimney in "L-shape" was built at the chamber dome to enable the free escape of excessive emission gas horizontally. Thus, the inner pressure in the chamber can be released to a large extent to the atmosphere. The flux of the free flow gas was measured by the flux sensor, which also measured the temperature, pressure and humidity at the same time. In case that the surface emission rate was lower than the suction rate of gas analyzers, sweep gas with a known flow rate would be injected into the headspace of the chamber to ensure a positive outflow at the flux sensor.

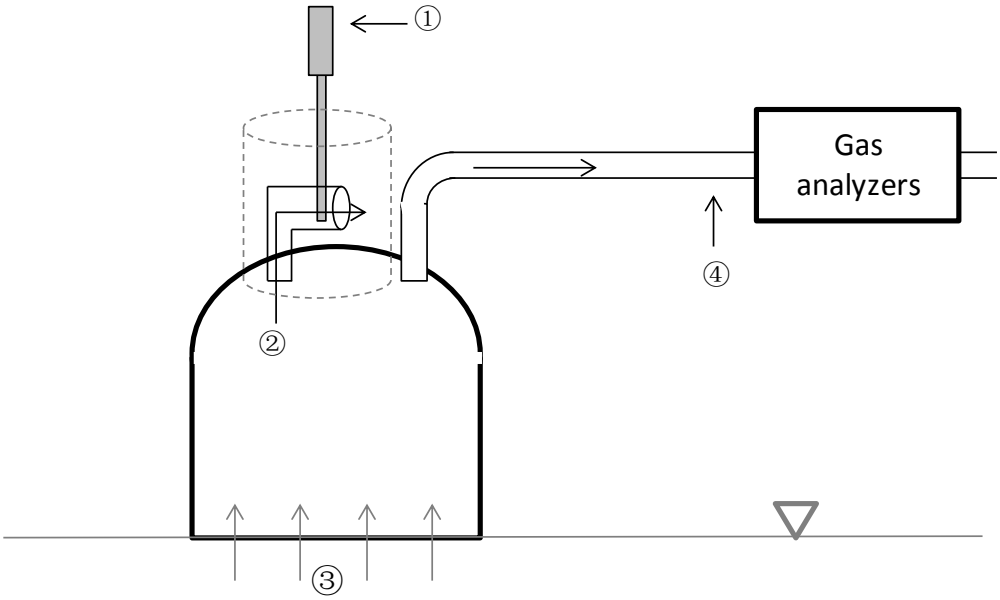


Figure 3.1. Schematic of the modified SEIFC. (1) Gas flux sensor; (2) "L-shape" chimney； (3) Advective surface off-gas emission; and (4) Teflon tubing connecting SEIFC and gas analyzers.

3.1.3. Mixed Liquor Characterization

Mixed liquor samples were collected adjacent to the modified SEIFC that represents the water quality of the certain area where sample gas was monitored. Water samples from the water surface were collected in order to compare with the surface emission. The analysis was conducted immediately upon the sample collection to prevent degradation.

Aqueous parameters analyzed included inorganic nitrogen species that involved in the biological nitrogen removal processes, i.e., ammonia, nitrite, nitrate. Due to the effect on the microbial activities, DO level was considered to be an important factor relating to N_2O emission and was monitored regularly. Dissolved N_2O levels in water samples were also measured as it could directly reflect the level of gaseous N_2O emission.

All the aqueous parameters were requested to test on site without standard laboratory conditions. Therefore, portable meters, sensors and chemical kits were used for the analysis. Nitrogen species were tested using *Hach* kits with corresponding Test 'N' Tube method. Portable DO meters (*Hach; Hanna*) were used to measure dissolved oxygen level of the samples. Dissolved N_2O in the sample wastewater was measured using an electrode micro-sensor (*Unisense, N_2O-R*). Calibration was conducted every time before sample analysis to ensure the accuracy of measurement.

3.2. Full-Scale WRP Monitoring

3.2.1. BNR in Changi Water Reclamation Plant

The biological nutrient removal process of CWRP is a modified BNR based on Barnard sequential process. The treatment modules consist of four parallel trains, three of which are combined with BNR process. Each train contains six parallel basins and each basin consists of four compacting anoxic zones and one aerobic zone, as shown in Figure 3.2. The flow directions are showed by the arrows and the anoxic zones are indicated by the shaded area. Usually there is one basin out of the six left empty for periodical maintenance and the other five basins are under normal working condition. Primary effluent enters the module together with the recycled activated sludge, which is distributed to all running basins. Effluent from the aerobic tank of the former basin continues to enter the anoxic tanks of the following basin and go through further treatment. The final secondary effluent exit from basin 6 and heads to the sedimentation tanks.

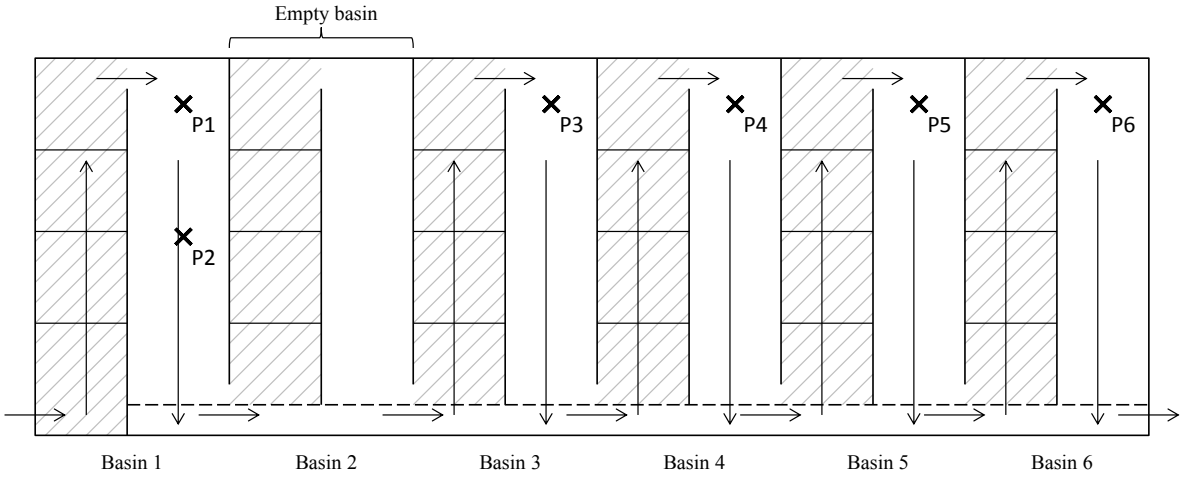


Figure 3.2. Sketch of BNR bioreactor (Train 2) in CWRP.

The designed length and width of the train is around 117 by 52m. With consideration of the wall thickness between the basins, the effective length and width of each basin is 50m and 24m, respectively. A single aeration tank has a dimension with length of 50m and width of 12m. The three parallel trains in the treatment module are under the same modality and operating condition, and one of them was chosen to conduct the monitoring.

The BNR reactors are entirely built underground in the liquid treatment building. The tanks are covered by concrete floor with manholes on it. Hence, the accessibility to the reactor was only through the several existing manholes. All the anoxic tanks were unable to be monitored because the launching of sampler at the anoxic zones was prohibited due to short distance of the sampling point to the mechanical mixers.

The nutrient level in the wastewater decreases along the six basins that may affect nitrous oxide emission. To get a comprehensive emission baseline, monitoring were conducted at all basins. Based on the limited accessibility, five monitoring points were chosen to locate at the inlets of the five functioning aerobic tanks. One more point was selected to be at the center of the aerobic tank of basin 1 for the comparison within one plug-flow tank as shown in Figure 3.2.

The overall monitoring lasted for six months from October of 2013 to March of 2014. During the monitoring period, regular continuous monitoring of 3~4 days per week were conducted at one of the selected points.

3.2.2. BNR in Ulu Pandan Water Reclamation Plant

The biological nitrogen removal process engaged in UPWRP is modified plug-flow BNR process. There are two treatment modules known as North Work and South Work (SW). The online monitoring was conducted at South Work. The SW consists of twelve parallel basins, of which one is left empty under maintenance. Primary effluent and returned activated sludge entering the module is distributed evenly to the eleven functioning basins. Each basin is one typical plug flow reactor that contains six bafflers. The first two channels are anoxic zones and the following six channels are aeration zone. The total eight channels were represented by CH0 to CH7 correspondingly (Figure 3.3).

The designed length of one basin at SW is 47.5m and the designed width is 33.4m. With consideration of baffler thickness, the width of each channel is 4.57m and the length is around 42.93m. The final channel connecting to the basin outlet has a length of 31m.

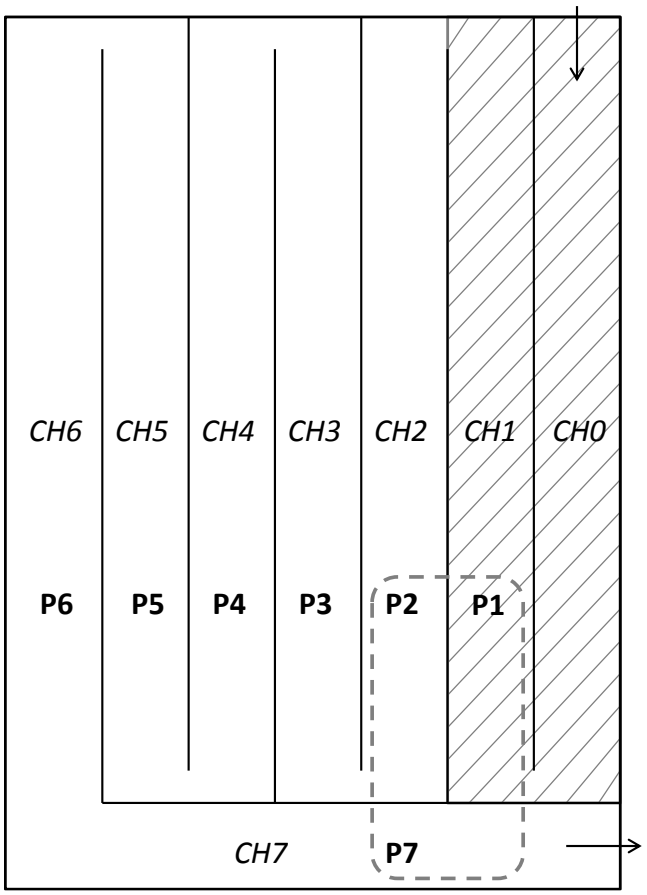


Figure 3.3. Sketch of one basin of BNR reactor in SW of UPWRP.

In a plug flow reactor, the nutrient level of the mixed liquor decreases along the flow direction. Because of the site condition and limitations, not all channels can be accessed by the monitoring setup. Among the accessible locations, seven monitoring points along the reactor were determined for water sample collection, indicated from P1 to P7 as shown in Figure 3.3. P1 was located at the center of the anoxic zone and the others were located at aerobic zone. From these seven points, three of them (P1, P2 and P7) at a relatively compacting area were selected for online gaseous monitoring. P2 was at the inlet of the aerobic zone and P7 was the effluent zone near the reactor outlet.

The overall monitoring lasted for three month from October of 2014 to December of 2014. Average online monitoring period was around 5 days at each point.

3.2.3. Odor Control System Monitoring

Both CWRP and UPWRP have air extraction systems and the odorous air is extracted to the air treatment system. Monitoring at the odor control systems was implemented in both plants. In CWRP the selected air duct for gas sampling contains emission gas from train 2 BNR processes and the following secondary sedimentation tanks. In UPWRP the selected air duct for gas sampling contains emission gas from BNR processes and secondary clarifiers of South Work.

The gas samples were pumped out from the air duct into 10-liter air bags owing to restricted accessibility of the online monitoring system. The N_2O concentration in the sample gas was analyzed offline by the gas analyzers.

3.3. Data Collection and Analysis

3.3.1. Advective flux Calculation

There is always excessive gas emission from an aeration tank so that the inner pressure could be kept positive inside the SEIFC chamber. Pure advective flow rate was calculated from the gas analyzers' suction rate and excessive flux

monitored at chamber outlet. The pure advective flux from the water surface can be calculated by the following equation (***Eq. 1***).

$$F = \frac{Q_S + f \cdot a}{A} \qquad (Eq.1)$$

where

F is advective flux of exhaust gas;

Q_S is sample flow rate of gas analyzers;

f is the flux measured by the gaseous flux sensor;

a is the cross sectional area of the chimney outlet; and

A is the bottom surface area of the SEIFC.

When monitoring an anoxic reactor, the status of the inner pressure of the SEIFC was affected by the actual emission condition. When the advective emission flow rate is sufficient to feed the sample flow of the analyzers, the calculation will be as same as it of aerobic reactor. In the situation that the advective gas emission is not sufficient to feed the gas analyzers, the ambient air will enter the chamber from the chimney and dilute the sample gas. The calculation of advective flux will be calculated by ***Eq.2***.

$$F = \frac{Q_S - f \cdot a}{A} \qquad (Eq.2)$$

At the same time, the actual nitrous oxide concentration in the sample gas will be calculated as:

$$C_E = \frac{Q_S \cdot C_S - f \cdot a \cdot C_A}{F \cdot A} \quad \textit{(Eq.3)}$$

where

C_E is the nitrous oxide concentration in emission gas;

C_S is the nitrous oxide concentration measured by gas analyzer;

C_A is the nitrous oxide concentration of ambient air near the SEIFC.

During monitoring, the SEIFC was floating on the wastewater surface, of which the bottom was sealed by water. The only opening connecting to ambient air that allowed free flow of emission gas was the small chimney. There was a tiny difference between the inner and outer pressure due to the shape of the floating chamber and the chimney's piping structure. When passing through the chimney, the gas pressure would decrease and the flow speed would increase accordingly, which was known as Venturi Effect. Therefore, the gaseous flux measured by the flux sensor would become slightly larger, resulting in a larger calculated results of the real advective emission rate. Simulating tests had been conducted to avoid the calculation error. A stable linear relationship had shown between the measured flux by the sensor and real gas emission rate which is shown in Figure 3.4.

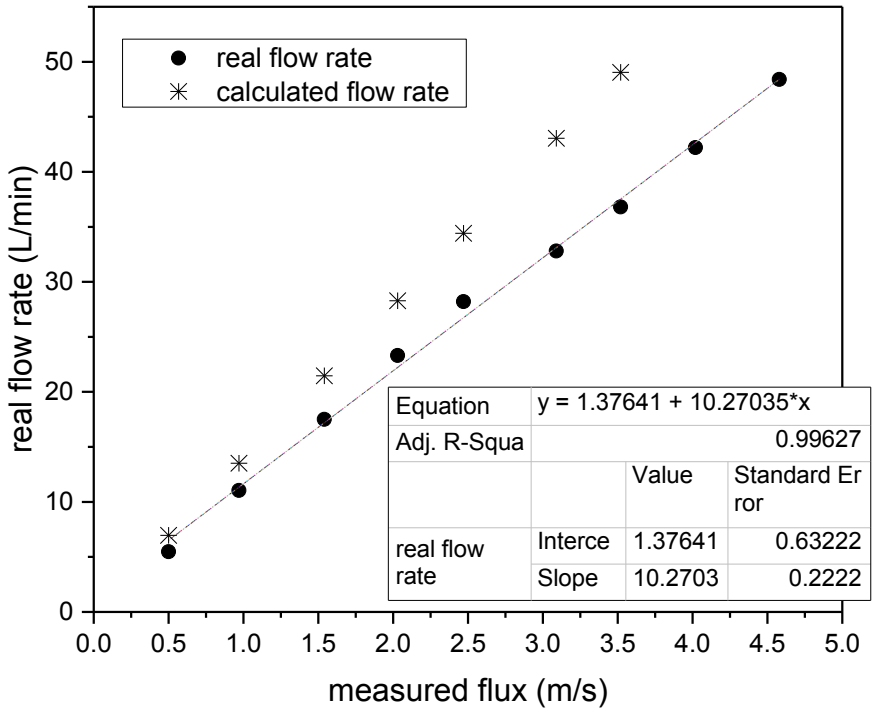


Figure 3.4. Relationship between real gas flow rate and calculated gas flow rate through the modified SEIFC.

The calculation of advective flux could be further developed as ***Eq.4***.

$$F = \frac{Q_S + 10.27f + 1.3764}{A} \qquad (Eq.4)$$

This effect is not likely to happen to the opposite case when ambient air freely flows back into the chamber, considering the sensor tip is near the chimney outlet that is not affected by the piping structure.

3.3.2. Nitrogen Greenhouse Gas Emission Estimation

The concentrations of N_2O and NO_x in gas samples were analyzed at real time by the analyzers and the data were transferred and recorded in the data logger. The gas samples represented the pure emission gas from the water surface in normal condition without flow back of ambient air. Total gas emission rate from the single tank can be estimated with known water surface area. The amount of total nitrogen GHG emitted comes from the tank could then be calculated accordingly.

The calculations were based on a few assumptions. Firstly, the microbial metabolism activities in the reactor were highly dynamic. Gas released at every single point on the water surface could contain different N_2O concentration. Practically, the N_2O concentrations in the emission gas from two points in the same tank with a close distance would not have a big difference. Assumption had been made that the N_2O concentration within the determined geometrical area were similar to each other. Furthermore, in aerobic tanks, the difference in aeration rate would affect the advective emission rate. Aeration rate would be decreasing slightly along the diffusers. The bubbling orientation will be changed by the water flow direction. Therefore, the calculations had assumed an evenly aeration intensity for all the reactors without consideration of the dead zones.

3.3.3. Monitoring Frequency

The analysis of nitrogen greenhouse gas concentrations was on a real time basis. Each monitoring session lasted for 2 to 7 days. Identically, the online flux measurement was done at similar frequency. The water sample collection was conducted either in the morning or afternoon. Repeat duplication/triplication had been done for each test.

Table 3.1. Daily monitoring frequency of online monitoring system

	Monitoring period	*Frequency of recording*	*Test method*
Flux of free flowed gas (m/s)	24-h	1 min	Online gaseous
Sampled gas flow rate (l/min)	24-h	1 min	Online gas analyzers
N_2O/NO_x concentrations (mg/m^3)	24-h	1 min	Online gas analyzers
Dissolved N_2O (mg/l)	-	Once/Twice a	Micro-sensor
DO (ppm)	-	Once/Twice a	Portable DO
NO_2-N (mg/l)	-	Once/Twice a	Hach kits
NO_3-N (mg/l)	-	Once/Twice a	Hach kits
NH_3-N (mg/l)	-	Once/Twice a	Hach kits

The sampling of gas from air duct was in a point-sampling mode. The sampling in CWRP was conducted around every 20~30min from 9:30am to 4:30pm. Each of the sampling duration was around 1min. The sampling in UPWRP was

conducted once a day either in the morning or afternoon with duration of 1min. Duplicated samples were taken for each sampling.

3.3.4. Correlation Analysis

The correlation analysis results were expressed by Pearson Correlation Coefficient (referred to as the PCC). In statistics, the PCC is a measure of the linear correlation between two variables, giving a value between +1 to –1 inclusive, where 1 is total positive correlation, 0 is no correlation and –1 is total negative correlation. The PCC is widely used as a measure of the degree of linear dependence between two variables. In this study, the PCC was calculated using the IBM SPSS Statistics on the measured aqueous and gaseous parameters, which was to explore the linear correlation between the mixed liquor characteristics and spontaneous N_2O emission from water surface of the treatment tanks.

Chapter 4: Studies on Changi Water Reclamation Plant

4.1. CWRP Loading

Average daily wastewater entering CWRP was 856,250 m^3/d. Taking account of the three BNR trains, the daily wastewater loading was about 642,188 m^3/d. The average TKN in the raw wastewater was 42 mg/L and the average TN in the effluent was 4.8 mg/L.

4.2. Online Monitoring Results

4.2.1. Advective Gas Emission Rate

Aeration rate in each aerobic tank was expected to be stable due to operational control. Figure 4.1 shows the monitored rate of gas emitted into the headspace of the SEIFC over a period of 3-day at P2. Within 24 hours, relatively steady gas emission rate from the mixed liquor surface can be observed. No significant fluctuation was observed during the 3 days.

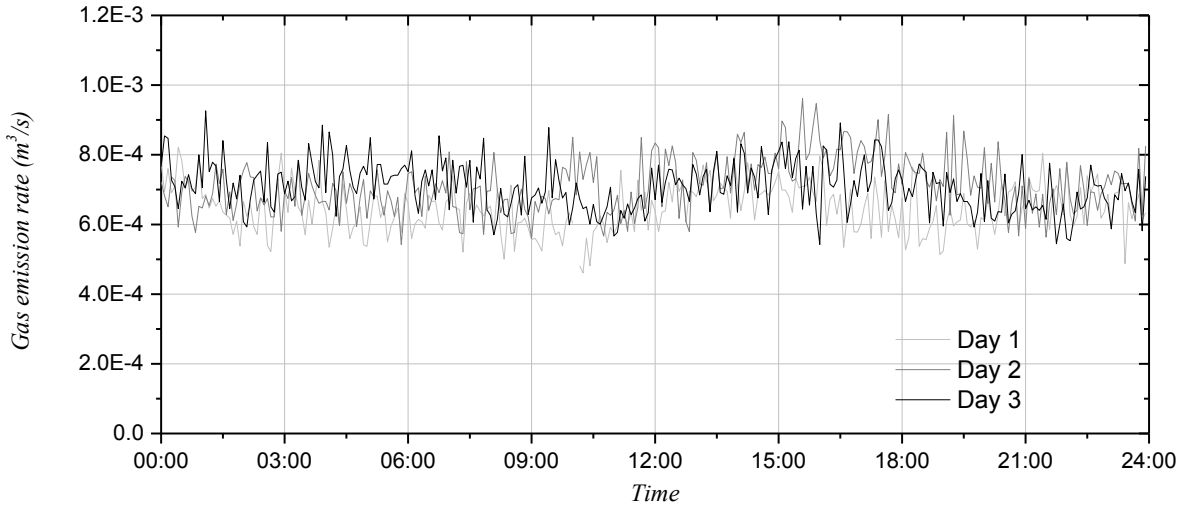


Figure4.1. Gas emission rate into the SEIFC headspace over 3 days at the center point (P2) of basin 1 at Train 2.

The gas emission rate in the aerobic tanks was mainly controlled by the aeration rate. The rate of gas generation by microbial metabolism could be negligible compared to that of aeration. The aeration rate was adjusted timely according to the COD concentration of the influent wastewater. When higher organic loading was detected from the wastewater, higher aeration rate would be provided, leading to higher gas emission. On the other hand, the DO in the treated water was required to be at a low level. Therefore, the aeration in the sixth basin was maintained at a comparably lower rate in order to control DO level in the effluent.

As expected, little difference of the surface flux was found at different locations within the same tank by comparing the headspace flow rate of P1 and P2. Therefore, the overall N_2O emission from one basin could be estimated based on the assumption that the exhaust gas was emitted evenly throughout the basin. Table 4.1 shows the average gas emission rate into the headspace of the SEIFC

and the overall advective fluxes from the aerobic zones of each basin. The first four basins had gas emissions within the range of 1 to 1.33 m^3/s per basin. The exhaust gas emission rate of the last basin was less than 0.67 m^3/s per basin. There were two reasons causing the significant low emission rate in basin 6 compared to other basins: firstly, the organic loading in the wastewater was significantly diluted in the last basin, therefore, the aeration demand in the basin was much lower; secondly, it was necessary to control the DO level in the secondary effluent to meet the criteria, hence, the aeration rate in basin 6 was controlled at a relatively low level. The overall daily gas emissions from each aerobic tank were shown in Figure 4.2.

Table4.1. Average exhaust gas emission rate into SEIFC and corresponding advective flux calculated of aerobic zones of each basin.

	Exhaust Gas Emitted into SEIFC (m^3/s)	***Average Advective Flux (m/s)***
Basin 1	0.00069	0.0018 ± 0.00013
Basin 3	0.00083	0.0021 ± 0.00026
Basin 4	0.00080	0.0020 ± 0.00009
Basin 5	0.00072	0.0019 ± 0.00030
Basin 6	0.00040	0.0010 ± 0.00022

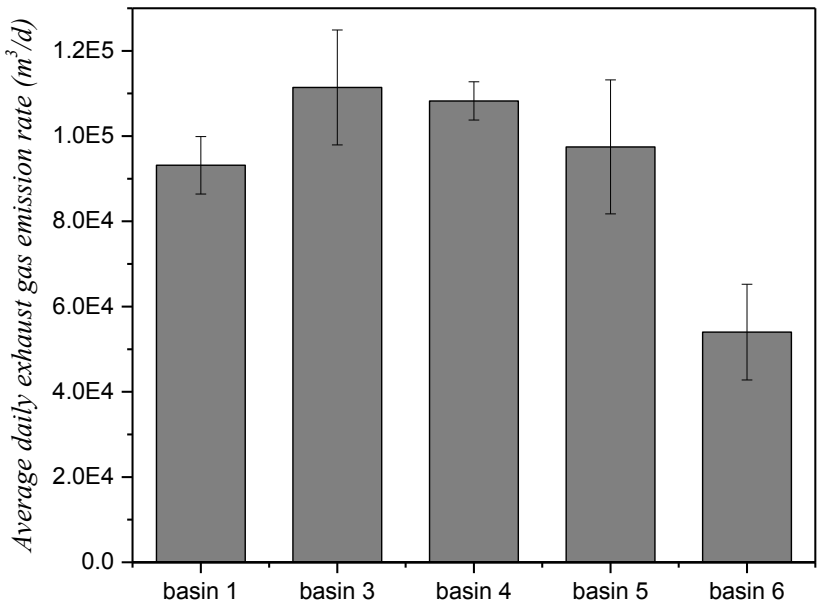


Figure 4.2. Daily gas emission from the aerobic zones of each basin.

4.2.2. N_2O and NO_x Concentration in Emission Gas

The N_2O concentration detected in the exhaust gas from the aerobic tank was found to vary within a certain range each day. Figure 4.3a shows the concentration of N_2O emitted over a four-day of continuous monitoring at the aerobic zone of the first basin (P2). The N_2O concentration decreased in the night and started to increase from the morning (6:00 to 8:00). There were two peaks occurring during the day. The first peak appeared during lunch time from 10:00 to 12:00, while the second peak occurred during dinner time between 18:00 to 20:00. Each peak period lasted two to three hours. This diurnal N_2O emission trend followed the domestic nutrient generation trend in the

wastewater. The time lag between the peaks detected in the secondary treatment process and the diurnal dining time was resulted from the transportation of municipal wastewater through the DTSS and primary treatment. At the meantime, the concentration of NO_x monitored in the exhaust gas followed a similar trend with that of the N_2O, of which the concentrations were relatively low (Figure 4.3b). From the monitoring results, up to 99% of the detected NO_x was NO, and the NO_2 concentration was negligible.

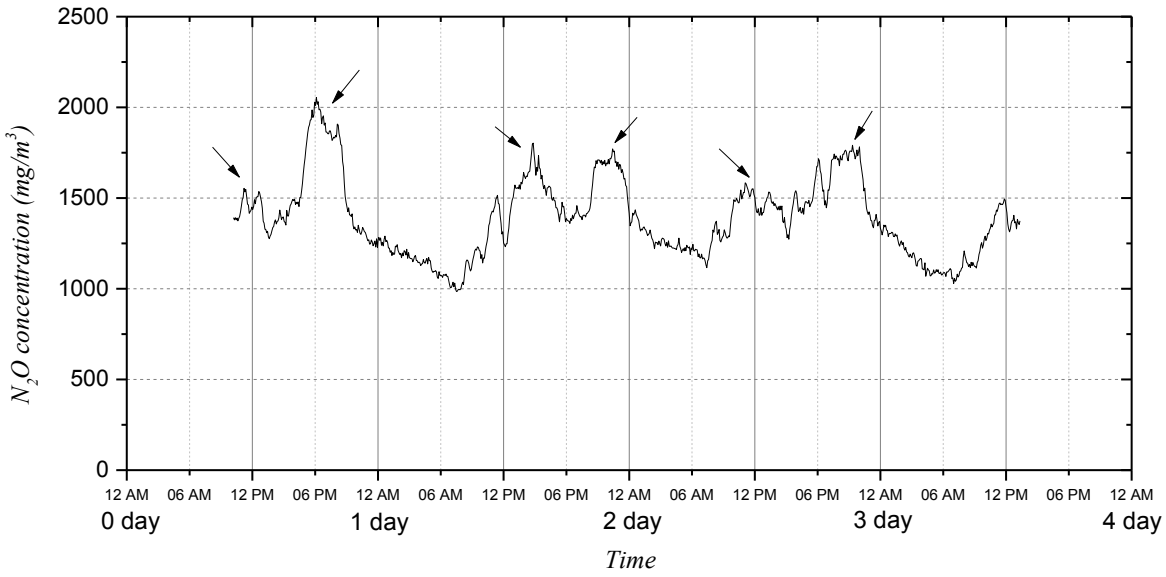


Figure 4.3a. Four-day profile of N_2O concentration in the emission gas monitored at the aerobic zone of basin 1 (P2)

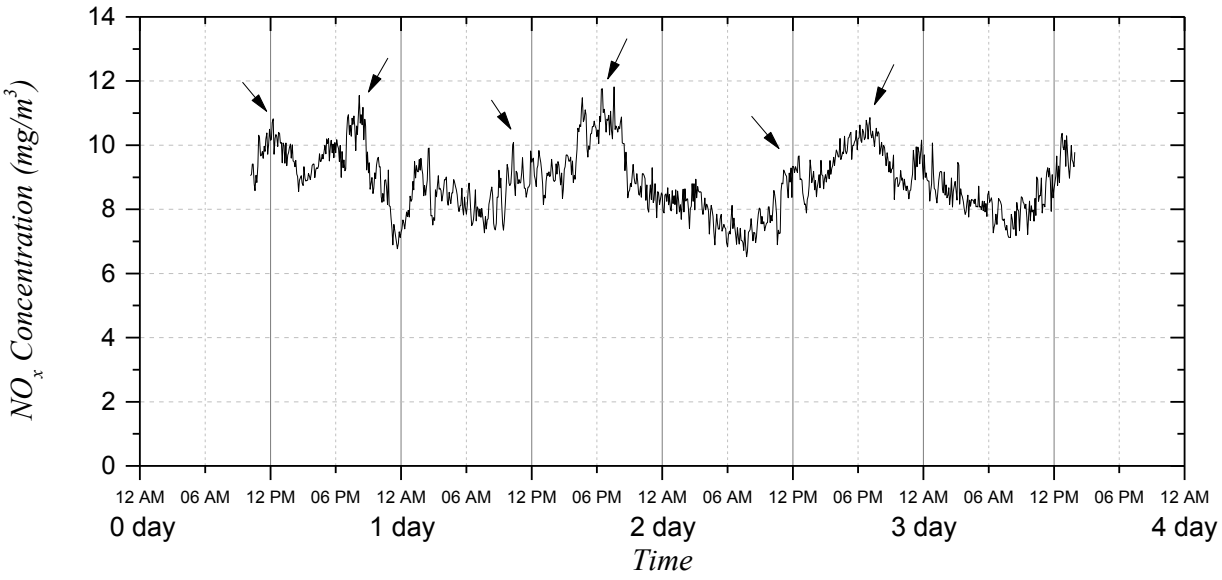


Figure 4.3b. Four-day profile of NO_x concentration in the emission gas monitored at the aerobic zone of basin 1 (P2)

The concentration of N_2O in the emission gas was observed to be decreasing along the train, which was affected by the nutrient level. N_2O concentration could reach as high as 1800 mg/m^3 in basin 1 and as low as 10 mg/m^3 in basin 6 (Figure 4.4a). Similarly, NO_x concentrations detected in the emission gas decreased along the reactor as well (Figure 4.4b). The 24-hr emission profiles of the same basin during different monitoring days were similar.

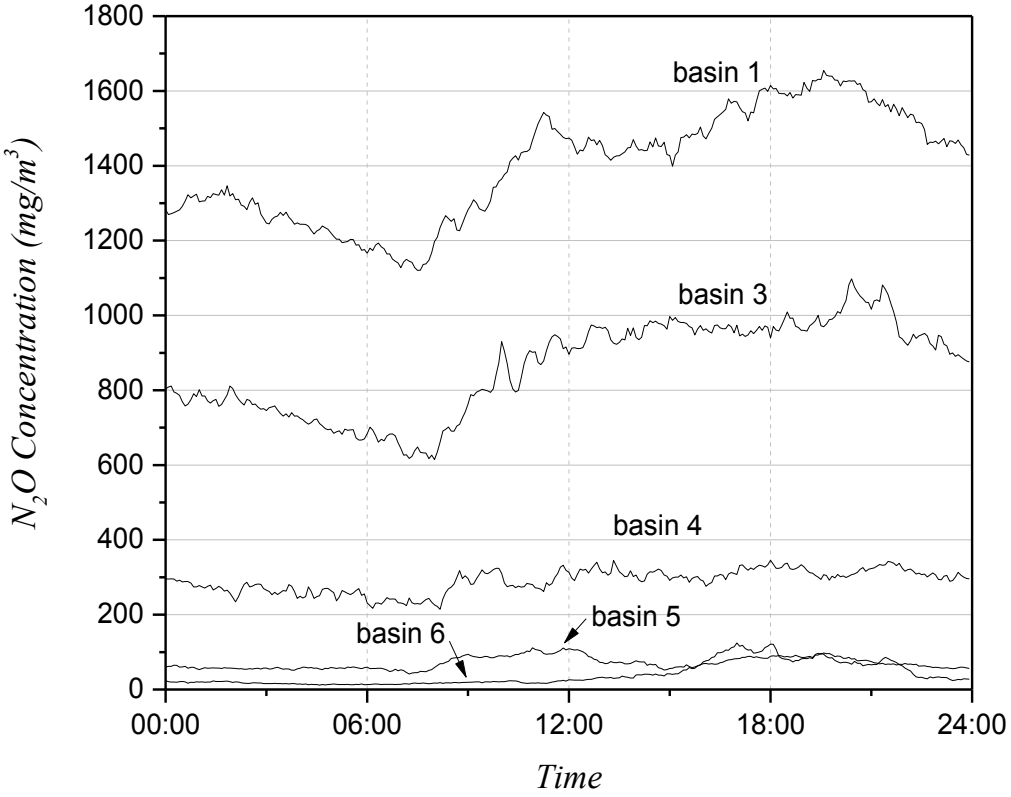


Figure 4.4a. N_2O concentrations in the emission gas from all five monitored basins.

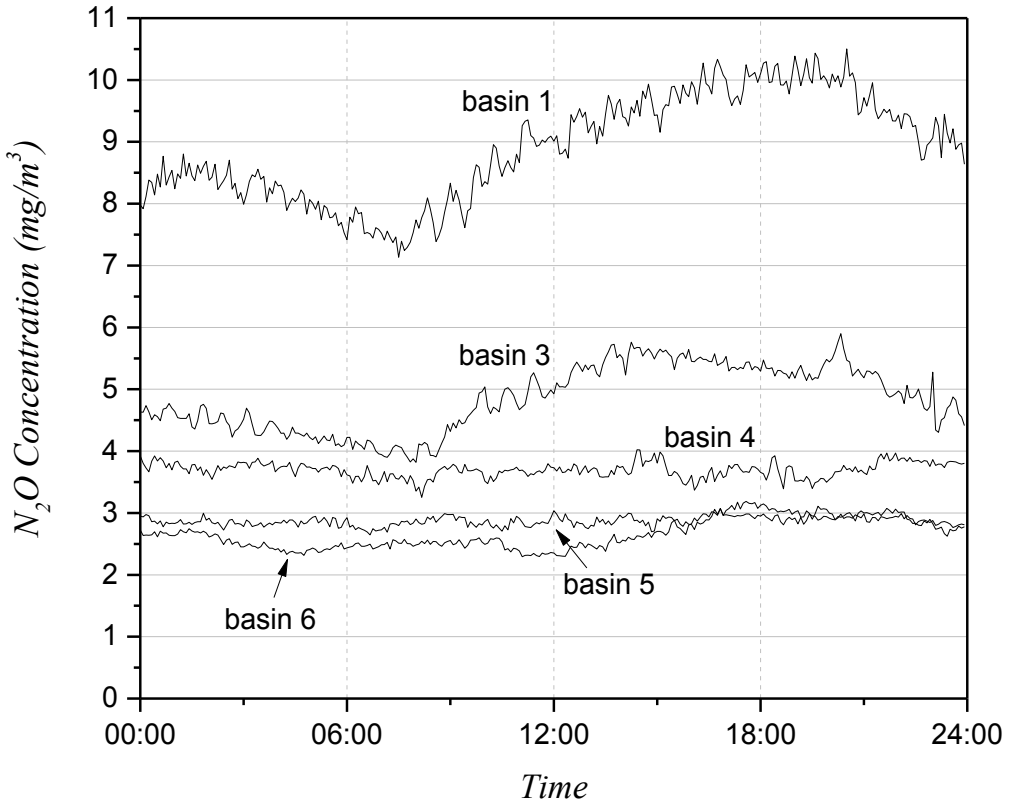


Figure 4.4b. N_2O concentrations in the emission gas from all five monitored basins.

4.3. N_2O and NOx Daily Emission

Mass fluxes of N_2O and NO_x emitted from each monitoring point were accounted by mass emission within a unit surface area per day (Table 4.2). The emission of both mass fluxes decreased from upstream to downstream due to decreasing nutrient level. There was no obvious difference in the mass emission from the first two monitoring points at basin 1. The N_2O mass flux emitted from the secondary sedimentation tanks should be similar to or even lower than the N_2O mass flux emitted from basin 6, which was almost a hundred times lower

than that of the first basin. Monitored mass fluxes of NO and NO_2 were rather negligible compared with that of N_2O. By calculation, over 90% of the exhaust nitrogen compounds from the aeration tanks were N_2O.

Table 4.2. Daily mass flux of N_2O and NO_x from each monitoring point.

Monitoring point	*Daily mass flux of N_2O ($g/m^2/d$)*	*Daily mass flux of NO_x ($g/m^2/d$)*
P1	209.9 ± 32.6	1.5 ± 0.078
P2	217.4 ± 10.0	1.4 ± 0.198
P3	157.1 ± 7.2	0.9 ± 0.064
P4	56.9 ± 6.1	0.7 ± 0.095
P5	11.4 ± 1.5	0.5 ± 0.029
P6	2.5 ± 1.2	0.2 ± 0.024

Estimations of daily N_2O and NO_x mass emissions from each basin are displayed in Table 4.3 and Figure 4.5. The overall N_2O and NO_x mass emissions represented the emissions from only the aerobic zones of the train. Considering the three BNR trains, the total estimated N_2O and NO_x emission from the aerobic zones of the BNR reactors were 794.74±67.20 and 6.831±0.706 kg/d, respectively.

Table 4.3. Average daily N_2O and NO_x emissions from each basin.

	Daily N_2O mass emission (kg/d)	*Daily NO_x mass emission (kg/d)*
Basin 1	128.19±12.77	0.874±0.083
Basin 3	94.24±4.29	0.547±0.064
Basin 4	34.16±3.69	0.438±0.057
Basin 5	6.84±0.92	0.281±0.017
Basin 6	1.48±0.73	0.136±0.015
Overall emission of train2	264.91±22.40	2.277±0.235

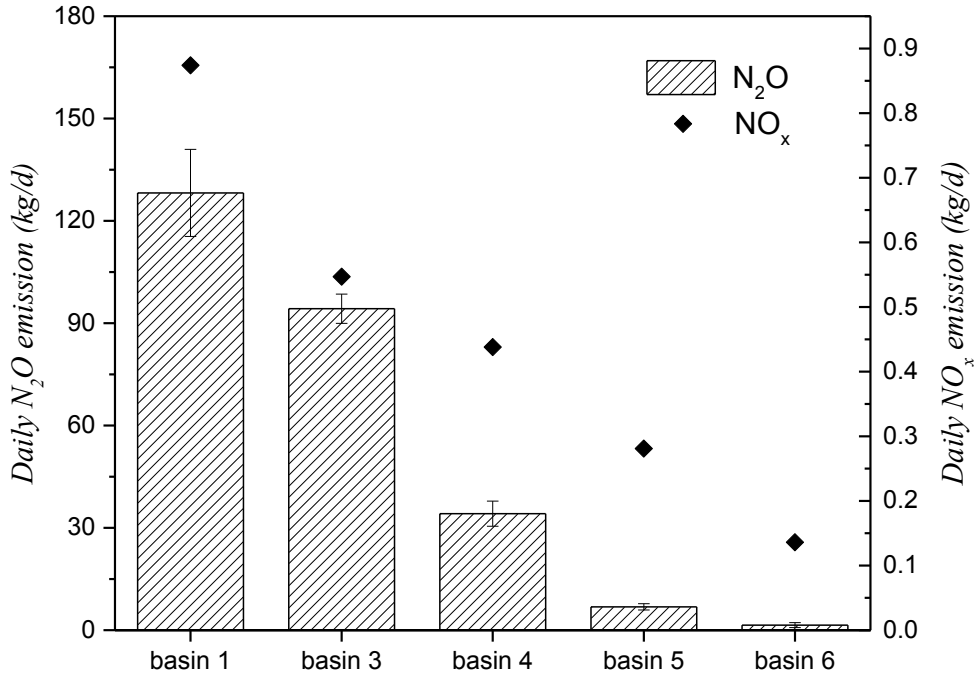


Figure 4.5. Average daily N_2O and NO_x emissions from five running basins.

4.4. N_2O Emission Fraction and Emission Factor

The emission fraction represents the conversion rate of nutrients into N_2O emission in a BNR process. The influent dissolved TKN used for calculation was monitored from the raw wastewater. The reason is that the dissolved TKN concentration between the raw wastewater and the influent of the secondary treatment is expected to be rather similar since the primary treatment before the BNR process could only achieve negligible nitrogen removal. The emission fraction of influent TKN emitted as N_2O was calculated to be 1.88±0.116%. The emission fraction of total removed nitrogen emitted as N_2O was calculated to be 2.12±0.18%.

The emission factor represented the average yearly N_2O mass emission per capita based on the population served by the wastewater treatment plant. The N_2O emission factor of the BNR process in the CWRP was calculated based on the aerobic zones, which was 0.051±0.004 kg N_2O/cap/yr. The population equivalent served by CWRP was calculated based on the water consumption equivalent reported by PUB in February of 2014, which was 151 L/cap/d. The converted emission factor as CO_2 equivalent was 15.86±1.34 kg CO_2 eq/cap/yr.

4.5. Correlation between Mixed Liquor Characteristics and N_2O Emission

4.5.1. Mixed Liquor Characteristics Analysis

The correlation between wastewater characteristics and gaseous N_2O emission had been studied during the online monitoring. Results of the parameters in the mixed liquor including DO, NH_3-N, NO_2-N, NO_3-N and dissolved N_2O, as well as the corresponding N_2O emission concentrations monitored at P2 are displayed in Figure 4.6. It was observed that the nitrite concentrations were much higher at the nitrification stage. Compared to nitrite level, nitrate and ammonia concentrations were relatively lower. This nitrite accumulating phenomenon in the aerobic zones might be resulted from inactive NOB metabolisms during the nitrification process while the AOB/AOA were comparably dynamic. This insignificant nitrification process behaved as partial nitrification or nitritation process. The accumulated nitrite during nitrification process in the mixed liquor could possibly lead to higher level of N_2O emission from anoxic zones.

Some of the aqueous parameters, i.e., NO_2-N, DO and dissolved N_2O, had decreasing concentrations with decreasing concentration of gaseous N_2O emission. A hypothesis was made that positive correlation might exist among these three aqueous parameters and the N_2O emission. The correlation between the aqueous parameters and N_2O emission will be further discussed in sections 4.5.2 and 4.5.3.

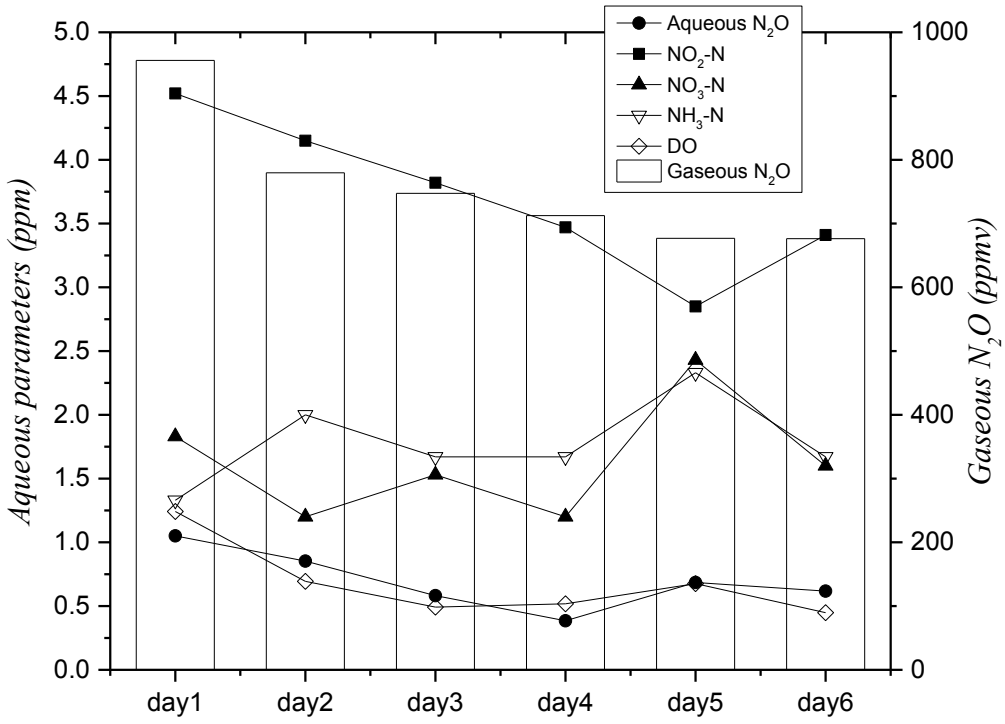


Figure 4.6. Mixed liquor characteristics measured at the centre point of basin 1 (P2).

4.5.2. Nitrate, Nitrite, Ammonia and DO

From the NO_2^-N, NO_3^-N, NH_3-Nand N_2O emissions measured throughout the five running basins, a rather obvious positive correlation between NO_2^-N and gaseous N_2O emissions could be observed (Figure 4.7). Compared to NO_2^-N, no obvious correlation could be seen between DO, NO_3-N, NH_3-N and N_2O emission.

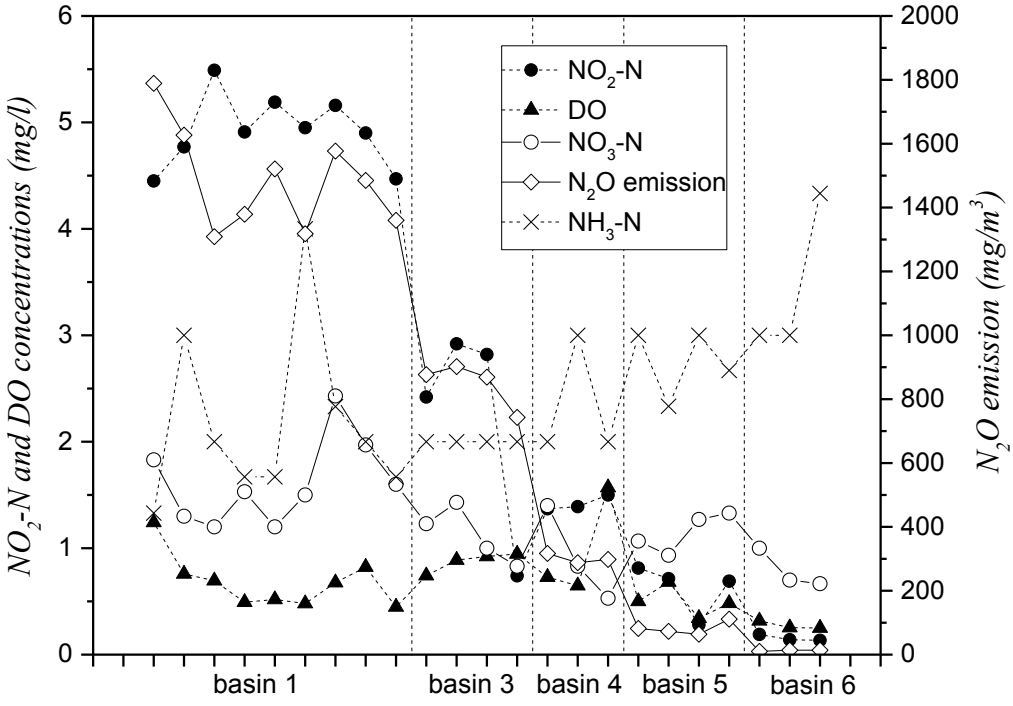


Figure 4.7. Comparison of aqueous parameters and N_2O gas emission through five running basins.

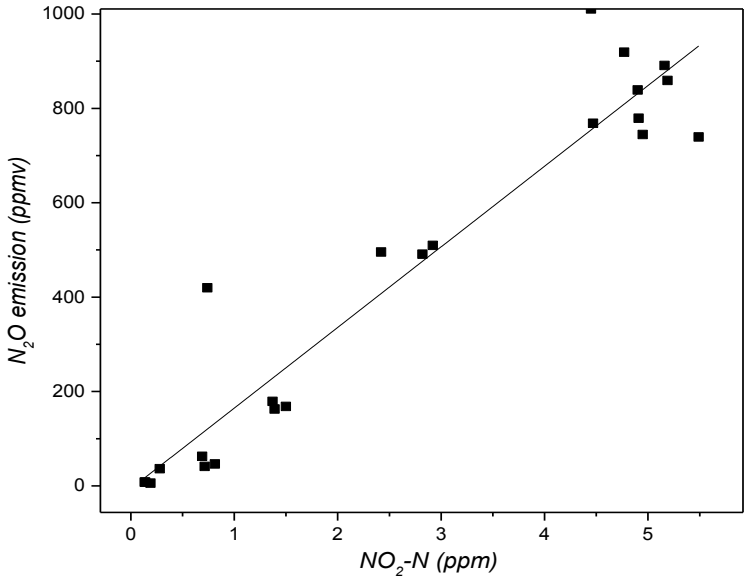
The Pearson Correlations among N_2O emission rate in the unit of ppmv and various aqueous parameters in the unit of ppm have been analyzed by SPSS (Table 4.4). The results showed that among all the aqueous parameters, nitrite has the most significant correlation with N_2O emission. The Pearson Correlation Coefficient (PCC) was 0.955 and the correlation was significant at the 0.01 level, indicating a strong linear correlation between the nitrite and N_2O emission. Nitrate has been also found to have a significant correlation with N_2O emission at the 0.01 level. However, the correlation coefficient was comparatively lower than that of nitrite. The linear correlations between N_2O and nitrite and nitrate calculated from existing data are shown in Figure 4.8 with slope and interception values displayed.

Table 4.4. Pearson correlations among N_2O emission and mixed liquor characteristics.

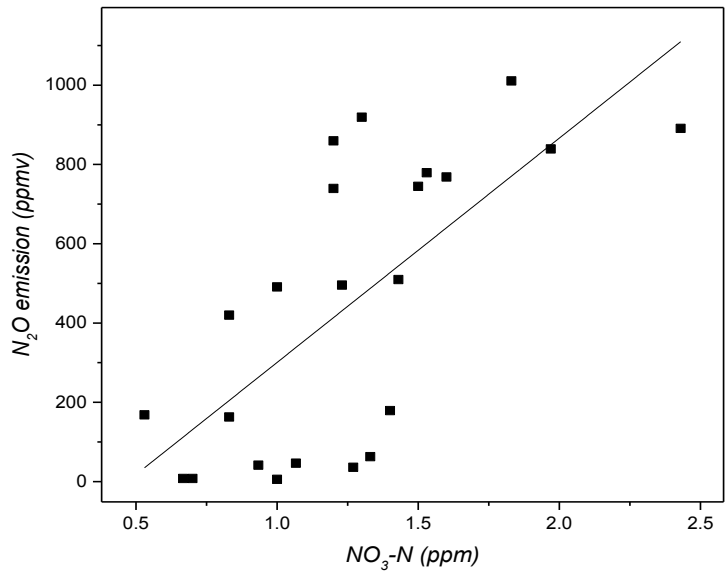
		N_2O gas	NO_2-N	DO	NO_3-N	NH_3-N
N_2Ogas	Pearson Correlation	1	.955**	.296	.692**	-.474*
	Sig. (2-tailed)		.000	.171	.000	.022
	N	23	23	23	23	23
NO_2-N	Pearson Correlation	.955**	1	.208	.678**	-.411
	Sig. (2-tailed)	.000		.342	.000	.051
	N	23	23	23	23	23
DO	Pearson Correlation	.296	.208	1	.027	-.554**
	Sig. (2-tailed)	.171	.342		.903	.006
	N	23	23	23	23	23
NO_3-N	Pearson Correlation	.692**	.678**	.027	1	-.330
	Sig. (2-tailed)	.000	.000	.903		.124
	N	23	23	23	23	23
NH_3-N	Pearson Correlation	-.474*	-.411	-.554**	-.330	1
	Sig. (2-tailed)	.022	.051	.006	.124	
	N	23	23	23	23	23

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).



	Value	Standard Error
Intercept	-5.97016	38.11478
Slope	170.86296	11.57004



	Value	Standard Error
Intercept	-265.09343	170.61488
Slope	565.80197	128.80126

Figure 4.8. Linear correlations between N_2O emission and NO_2-N and NO_3-N.

4.5.3. Dissolved N_2O

The dissolved N_2O concentrations in the mixed liquor were highly dynamic over the period of this study (Figure 4.9). Besides incoming wastewater characteristics and microbial activities, aeration rate was another important factor that affected the dissolved N_2O concentration in the mixed liquor as aeration strips the dissolved gas into the gaseous phase.

The concentrations of dissolved N_2O and spontaneous N_2O emission measured at P2 in either morning or afternoon were illustrated in Figure 4.9. The aqueous and gaseous N_2O concentrations presented similar trends during the study period.

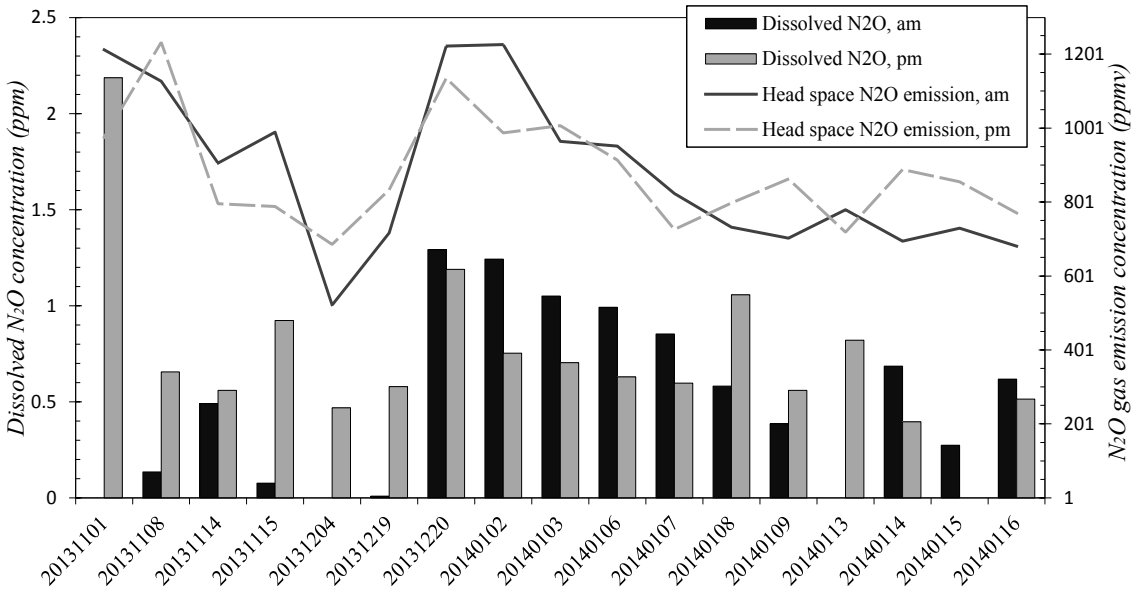


Figure 4.9. Comparison of dissolved N_2O in surface of the mixed liquor and N_2O gas emission monitored at the centre of basin 1 (P2).

According to Henry's Law, dissolved N_2O concentration is expected to be a direct indicator of N_2O gas emission from the surface of mixed liquor. However, the correlation between the dissolved N_2O and emitted N_2O in this current study was not as significant as expected. This may be due to the highly dynamic concentrations of the dissolved N_2O in the mixed liquor, which may be affected by multiple factors such as temperature and air stripping. The correlation was found to be significant at the 0.05 level from the SPSS analysis, where the PCC was 0.375 (Table 4.5). The significance was much lower than other aqueous parameters.

Besides the quality of the mixed liquor and microbial activities, solubility of N_2O could also be affected by temperature and N_2O partial pressure in the ambient air. This makes dissolved N_2O concentration more sensitive to the environment and more dynamic compared to other aqueous parameters.

Table 4.5. Pearson correlation between dissolved N_2O and emitted N_2O.

		DissolvedN_2O	EmittedN_2O
DissolvedN_2O	Pearson Correlation	1	.375*
	Sig. (2-tailed)		.032
	N	33	33
EmittedN_2O	Pearson Correlation	.375*	1
	Sig. (2-tailed)	.032	
	N	33	33

*. Correlation is significant at the 0.05 level (2-tailed).

4.6. Monitoring at Odor Control System

Gas samples were taken from the air duct located at the inlet of the odor control system of train 2. The designed pumping rate in a single air duct was 870~1155 m^3/min. The actual air flow rate in the air duct was measured to be 880 m^3/min. Two sessions of gas sampling from the air duct were carried out in July 2014 and January 2015, respectively. The calculated N_2O emissions from the air duct are listed in Table 4.6.

Table 4.6. N_2O emission fraction estimated from air duct monitoring.

Sampling time	*Average N_2O concentration in air duct (mg/m^3)*	*Estimated N_2O emission fraction of bioreactor (% of influent N)*
Jul 2014	462.42	4.61
Jan 2015	282.51	2.36

The N_2O emissions measured from the air duct were much higher compared to those obtained from the online monitoring. A major reason was that the online monitoring covered only the aerobic zones, while the odor control system took into account emissions from both the anoxic and aerobic zones, as well as the secondary sedimentation tanks. The secondary sedimentation tanks could be speculated to have insignificant contribution to the total emission due to the low emission monitored from the final effluent. The big discrepancy in the monitored emission fractions reflected that the anoxic zones might have big

contribution in the total N_2O emission. However, this conjecture will need to be proved by further monitoring.

The variation of N_2O emission in the two monitoring sessions from the air duct could be due to different wastewater quality, especially the nitrite content in the bioreactor. Figure 4.10 shows the average nitrite and nitrate concentrations in the bioreactor during the two monitoring sessions. The process behaved a more complete nitrification in Jan 2015, possibly due to changes in the microbial constitution and activities. The decreased nitrite concentration reflected less N_2O emission, which was consistent with the positive correlation between nitrite and N_2O emission observed during the online monitoring.

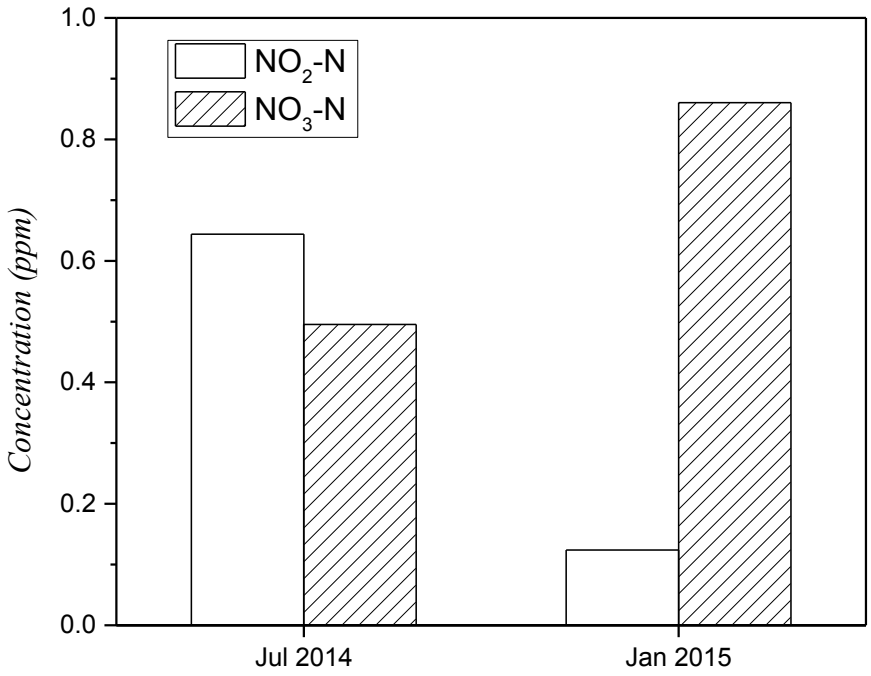


Figure 4.10. Average nitrite and nitrate levels in the bioreactor in Jul 2014 and Jan 2015.

4.7. Discussions

The prototype for online N_2O monitoring from the full-scale BNR processes at the CWRP was capable to obtain the diurnal variability of N_2O emission by 24-hr monitoring. However, this study did not monitor the effect of seasonal changes in N_2O emission on a yearly basis due to time limitation. It was relatively challenging logistically to conduct a comprehensive yearly study on the N_2O emissions.

After six months of monitoring in CWRP, N_2O emission baseline from the aerobic zones of the BNR process using the modified SEIFC was obtained. N_2O concentration in the emission gas was found to be the highest at the beginning location of the bioreactor and decreased along the train. The N_2O emission at the effluent was almost a hundred times lower than that at the influent portion. The amount of NO_x emission was negligible compared to N_2O emission.

The emission fraction of total influent nitrogen emitted as N_2O was 1.88±0.116% at the aerobic zone and the emission fraction of total removed nitrogen emitted as N_2O was 2.12±0.18%. Monitoring results of earlier studies on N_2O emission from full-scale BNR processes in other countries are listed in Table 2.1, of which the N_2O emission fraction varied from 0 to 25%. Although within an acceptable range, the overall N_2O emission fraction of 1.88±0.116% from the aerobic zones of the BNR processes in the CWRP was relatively higher compared to the results reported in previous monitoring studies. It has been observed from the mixed liquor characteristics that the nitrification process in

the aerobic zones behaved as partial nitrification with high nitrite concentration. Three recent studies have reported that N_2O emission level from partial nitrification could be higher than that of the full nitrification process (Ahn et al., 2011; Rodriguez-Caballero et al., 2013; Wei et al., 2014). The partial nitrification in the aerobic zone could be one reason resulting in accumulated $NO_2^-$and increased N_2O emission during the monitoring period. Therefore, current N_2O emission has the potential to be reduced if the BNR process achieves full nitrification instead of partial nitrification. The N_2O emission was expected to be lower after six months of the online monitoring when a more complete nitrification was observed.

Outstanding positive correlation between N_2O emission and nitrite concentration in the mixed liquor has been observed. This correlation observed was identical with the finding from earlier studies on N_2O emission in full-scale WWTPs (Chandran, 2012; Foley et al., 2010; Kampschreur et al., 2009, 2008b; Sümer et al., 1995). Correlation between N_2O emission and nitrate concentration has also been observed. However, the correlation with nitrate was not as significant as that with nitrite.

The amount and quality of daily domestic wastewater generation, as well as the operational conditions of the biological process could directly affect the amount of N_2O emission from the full-scale WRP. Seasonal variability of N_2O emission could be impacted by temperature fluctuation and precipitation. For Singapore, the temperature over the year is relatively constant, while the quality of wastewater entering the CWRP was strongly affected in the rainy season due to

storm water intrusion. Consequently, the nutrients level in the wastewater would be lower, resulting in less N_2O emission.

Overestimation or underestimation of the yearly N_2O emission might be caused by various factors. For the CWRP, the monitored baseline was not representative of the overall N_2O emission of the BNR process since the anoxic zones were not taken into account. If the anoxic zones are included, the real emission of the whole BNR process should be higher than the calculated values.

Chapter 5: Studies on Ulu Pandan Water Reclamation Plant

5.1. UPWRP Loading

The average daily wastewater flow entering the South Work of the UPWRP was 183,000 m^3/d. The average TKN in the raw wastewater was 44 mg/L and the average TN in the effluent was 11.6 mg/L.

5.2. Online Monitoring Results

5.2.1. Advective Gas Emission Rate

Similar to the CWRP, the advective exhaust gas emission from the bioreactor was relatively stable without significant fluctuation during a day. Figure 5.1 shows the rate of exhaust gas emitted into the SEIFC. Compared to those at the CWRP (Table 4.1), the exhaust gas emissions from the aeration tanks of BNR process in the UPWRP were lower.

The average gas emission rate from the mixed liquor near the effluent exit location (P7 in Figure 3.3) was slightly higher than that near the influent location (P2 in Figure 3.3), which may lead to higher DO level at the effluent exit location. Comparably, gas emission from the anoxic zone was much lower where the emitted gas was produced from microbial activities.

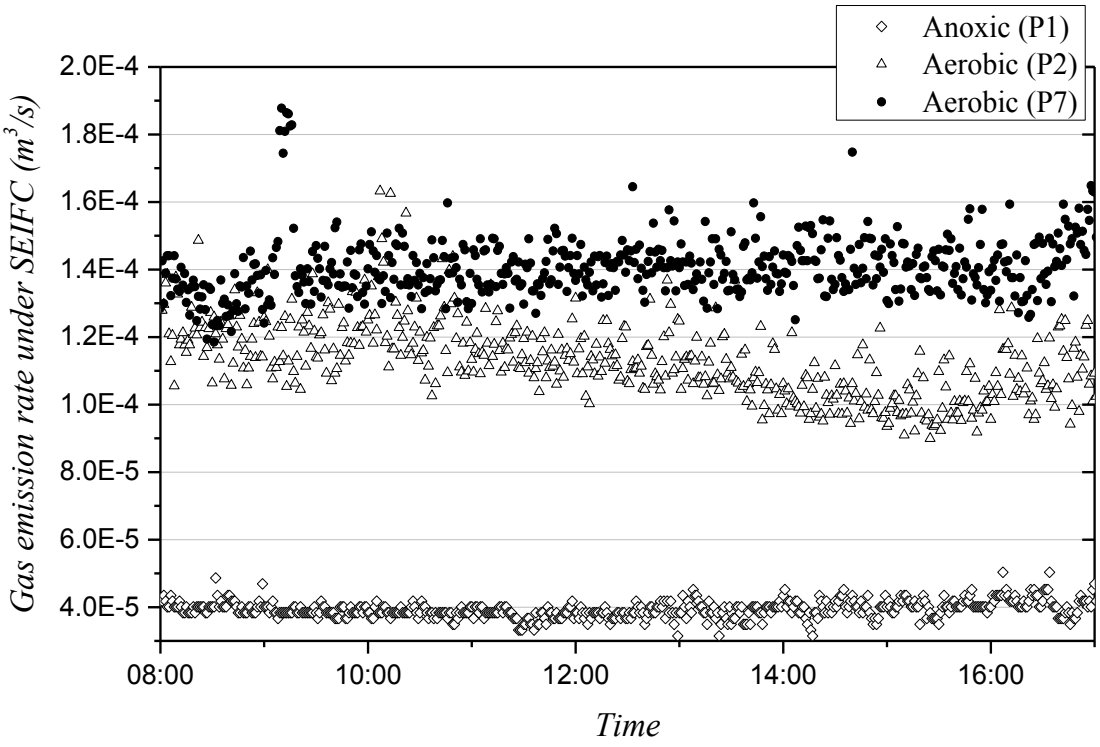


Figure 5.1. Gas emission rate from the bioreactor at monitoring point P1, P2 & P7.

5.2.2. N_2O and NO_x Concentration in the Emission Gas

As a whole, the average N_2O concentration in the exhaust gas from the BNR reactor in the UPWRP was much lower than that in the CWRP. The highest N_2O concentration was observed at P2 with peak concentration of around 70 mg/m^3 (Figure 5.2). Likewise, there were two peaks in the N_2O concentration detected from the beginning of the aerobic zone during the day. The two peaks were observed during 8:00 to 10:00 and 18:00 to 22:00. The occurring time of the peaks were similar with those observed in the CWRP, further confirming the

previous inference. N_2O emissions at the effluent of the aerobic zone were relatively lower due to decreasing nutrient level.

Compared to the aerobic zone, N_2O concentration in the exhaust gas from the anoxic zone was found to be much lower. This might be resulted from the high solubility of N_2O gas compared to nitrogen gas when they are produced from the denitrification process. Meanwhile, there is no bubbling in the anoxic zones to mechanically strip the dissolved N_2O from the liquid to the gaseous phase.

The average NO_x concentration in the emission gas from the aerobic zones ranged from 0 to 10 ppm, which was similar with that in the CWRP. It has been found that the NO_x concentration in the anoxic zone was relatively higher than that in the aerobic zone. In contrary with the N_2O concentration, the highest NO_x concentration in the emission gas was observed at P1 and the lowest was observed at P2 (Figure 5.2b). The higher NO_x concentration at P1 could be due to the existing of denitrification in the anoxic zone, during which the NO is an obligatory intermediate. A possible reason that P2 had the lowest NO_x concentration could be that the aeration rate at P2 was lower than at P7, resulting in relatively lower NO production and lower stripping rate during the nitrification process.

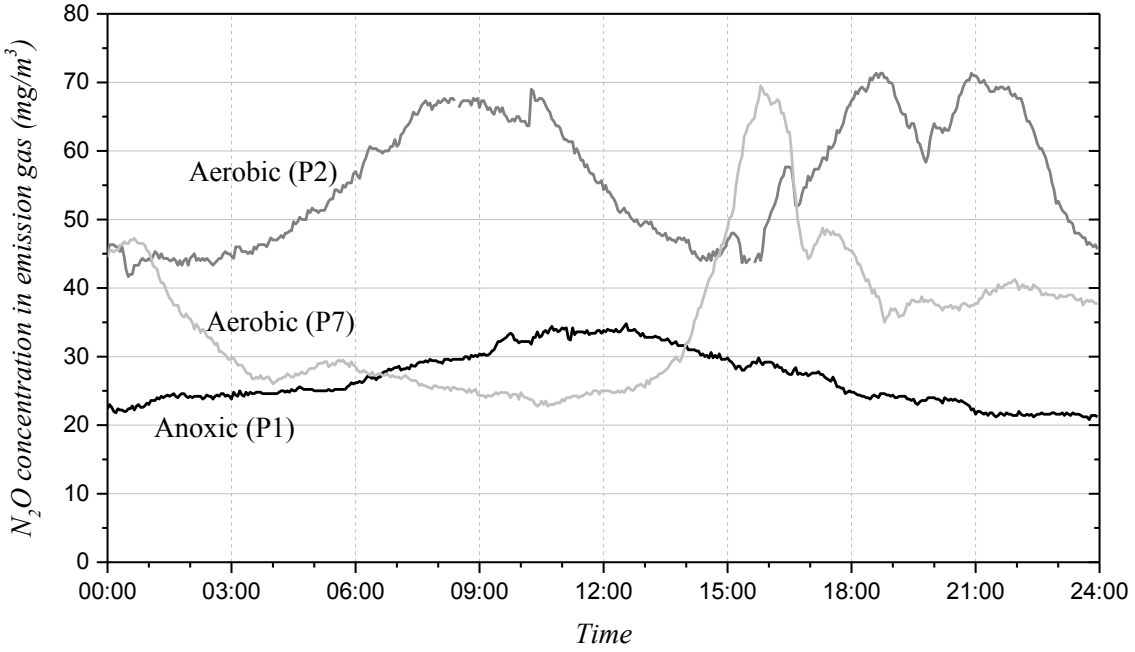


Figure 5.2a. 24-hour profile of N_2O concentrations in the emission gas monitored at P1, P2 & P7.

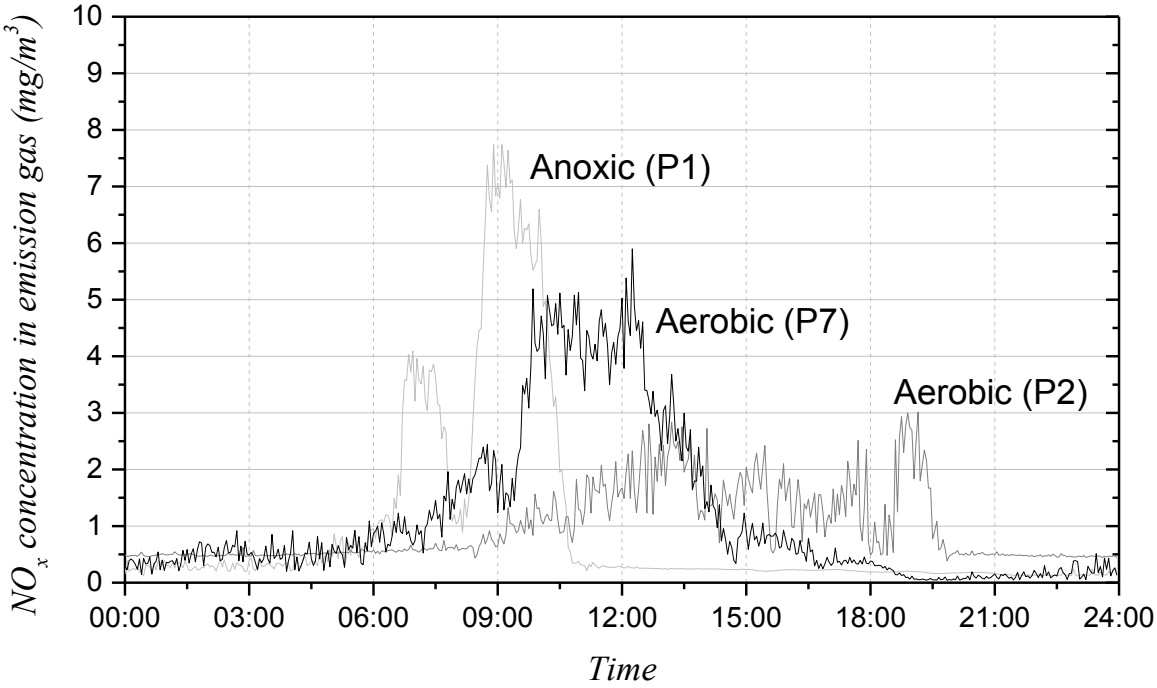


Figure 5.2b. 24-hour profile of N_2O concentrations in the emission gas monitored at P1, P2 & P7.

5.3. N_2O and NO_x Daily Emission

The mass fluxes of both the N_2O and NO_x emitted from the aerobic zones at P2 and P7 were much lower than the values monitored in the CWRP owing to exhaust gas emission containing low N_2O and NO_x content. Compared to the BNR process in the CWRP, the average N_2O mass flux monitored in the UPWRP was much lower than any of the basins monitored in the CWRP. Likewise, anoxic zones contributed to less N_2O and NO_x emissions than aerobic zones because of less air stripping.

Table 5.1. Average daily mass flux of N_2O and NO_x from each monitoring point.

Monitoring point	*Daily mass flux of N_2O ($g/m^2/d$)*	*Daily mass flux of NO_x ($g/m^2/d$)*
P1	0.234 ± 0.027	0.015 ± 0.007
P2	1.611 ± 0.201	0.064 ± 0.003
P7	1.248 ± 0.273	0.039 ± 0.015

An estimation of the daily N_2O and NO_x emissions from CH1, CH2 and CH7, where the three monitoring points were located, were calculated. It was obvious to see from Figure 5.3 that the beginning of the aerobic zone contributed to more N_2O emission than at the effluent exit zone. Anoxic zones' contribution to N_2O emission was much lesser than that of the aerobic zones. It was found that about

3.8% of the total mass of NO_x emission was attributed to N_2O emission, suggesting that NO_x emission was negligible.

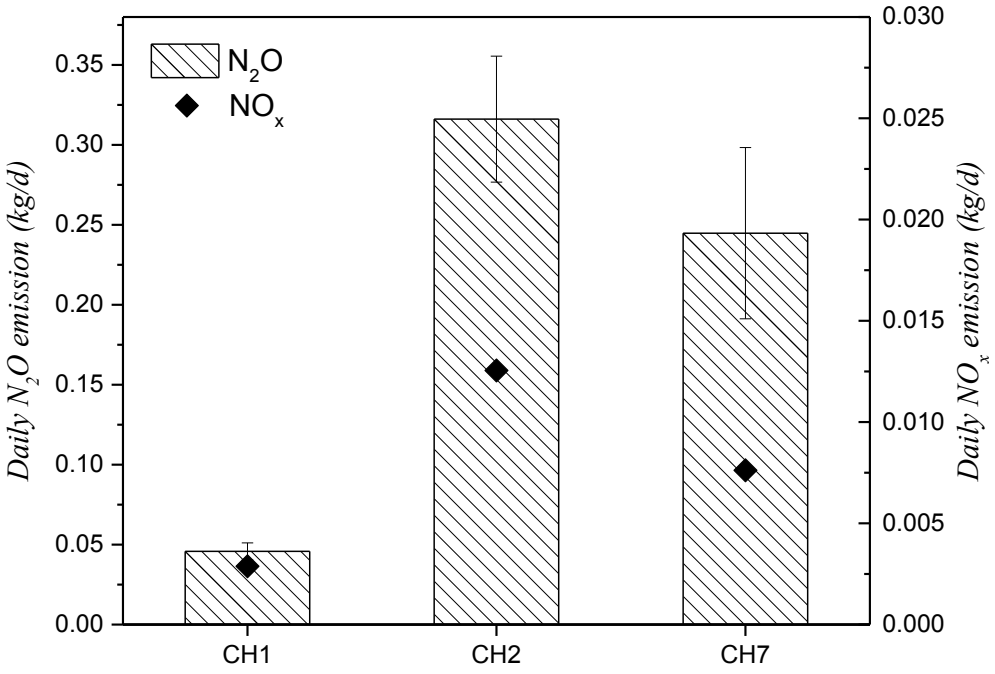


Figure 5.3. Estimation of daily N_2O and NO_x emission from CH1, CH2 & CH7.

The N_2O emissions from the channels that were not monitored were estimated based on the assumption that the mass fluxes of the emitted N_2O were similar as the monitored channels. This assumption would underestimate the total N_2O emission, which will be discussed in session 5.7.

5.4. N_2O Emission Fraction and Emission Factor

The overall N_2O emission from the basin was estimated to be 1.94±0.30 kg/d. Of the total N_2O emission, 4.48% was from the anoxic zones and 95.52% was from the aerobic zones. The emission of entire South Work containing 11 parallel basins was estimated to be 21.29±3.25 kg/d. The N_2O emission from channel 0 was estimated using the N_2O emission data monitored from channel 1. The N_2O emissions from channel 3 to 5 were estimated using the N_2O emission data monitored from channel 2. The N_2O emission from channel 6 was estimated using the N_2O emission data monitored from channel 7. The conversions of the N_2O emission estimation were based on the dimensions of each channel. The estimation of overall emission from the South Work was based on the assumption that the other 10 running basins have the same emissions with the monitored basin.

The N_2O emission fraction of influent TKN of the South Work at the UPWRP was 0.168±0.026%, while the N_2O emission fraction of the TN removed was 0.228±0.035%.

The emission factor represented the average yearly N_2O mass emission per capita based on the population served by the plant. The N_2O emission factor of the South Work at the UPWRP was 0.0064±0.0010 kg N_2O/cap/yr, which was equivalent to 1.987±0.303 kg CO_2 eq/cap/yr. The population equivalent was calculated based on water consumption rate of 151 L/cap/day (PUB, 2014).

5.5. Correlation between Mixed Liquor Characteristics and N_2O Emission

5.5.1. Mixed Liquor Characteristics Analysis

Mixed Liquor samples were collected from the 7 points along the plug flow reactor from upstream to downstream (P1 to P7 displayed in Figure 3.3). Results of the ammonia, nitrite, nitrate and DO concentration of the mixed liquor at the seven points are showed in Figure 5.4. Within the anoxic zone (P1), the mixed liquor contained high ammonia concentration that came from the primary influent and low nitrate concentration that came from the recycled activated sludge. Once the primary influent entered the aerobic zone, the ammonia concentration decreased sharply as it is being converted to nitrite and nitrate. The nitrate concentration increased in the aerobic zones and reached the highest concentration at the effluent exit point while the ammonia concentration decreased to zero. The nitrite concentration rose within the aerobic zones as an intermediate of nitrification and was totally converted to nitrate at the effluent exit point. The wastewater characteristics indicated that stable and complete nitrification and denitrification occurred in the bioreactor.

The DO concentration was found to increase from the aerobic zone and reached the highest concentration at the effluent exit point. The DO concentration at P7 was much higher than the concentration at P2 due to higher aeration rate, validating the speculation in section 5.2.1.

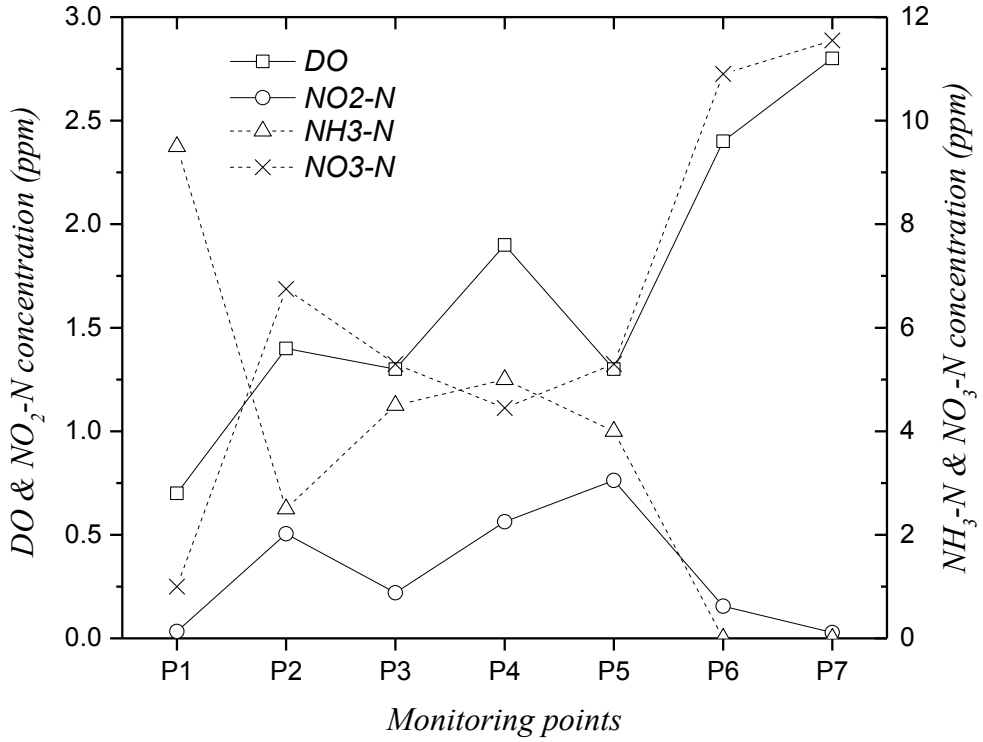


Figure 5.4. Mixed liquor characteristics measured at seven points of the bioreactor.

Dissolved N_2O in the wastewater along the bioreactor was found to be at very low concentration. The dissolved N_2O concentration was relatively higher in the anoxic zone and decreased sharply in the aerobic zone as shown in Figure 5.5. At most of the time the dissolved N_2O concentration was too low and non-detectable by the micro-sensor, especially for samples from the aerobic zone. This might be because during nitrification process, little N_2O was produced compared with denitrification process. Furthermore, the bioreactor was exposed to high outdoor temperature during the day, which could be as high as 34ºC. As a result, the solubility of N_2O decreased and the N_2O could escape from the mixed liquor (Weiss and Price, 1980).

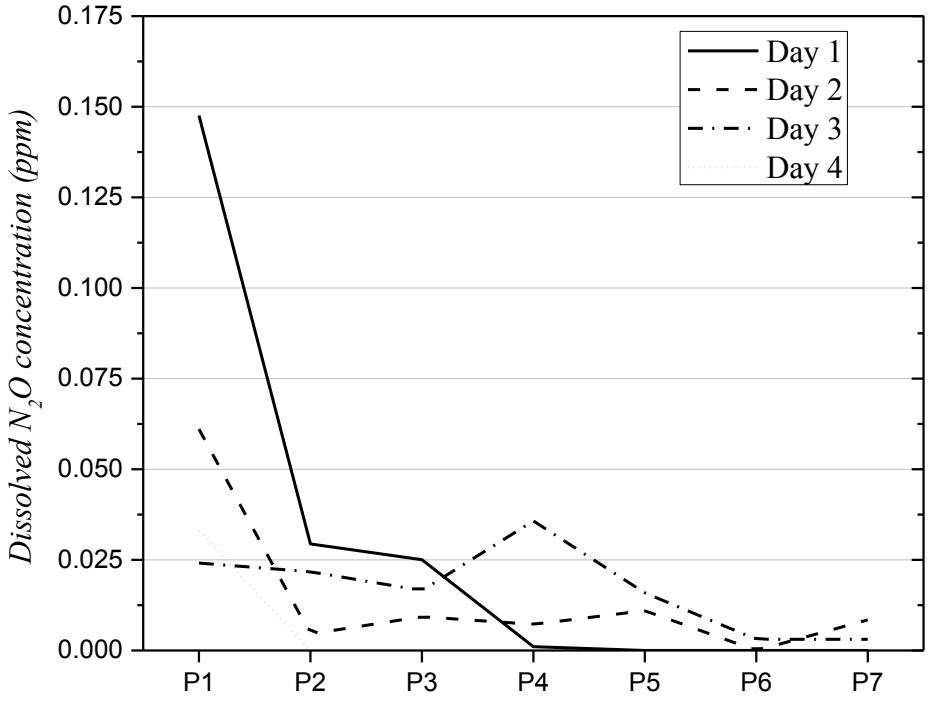
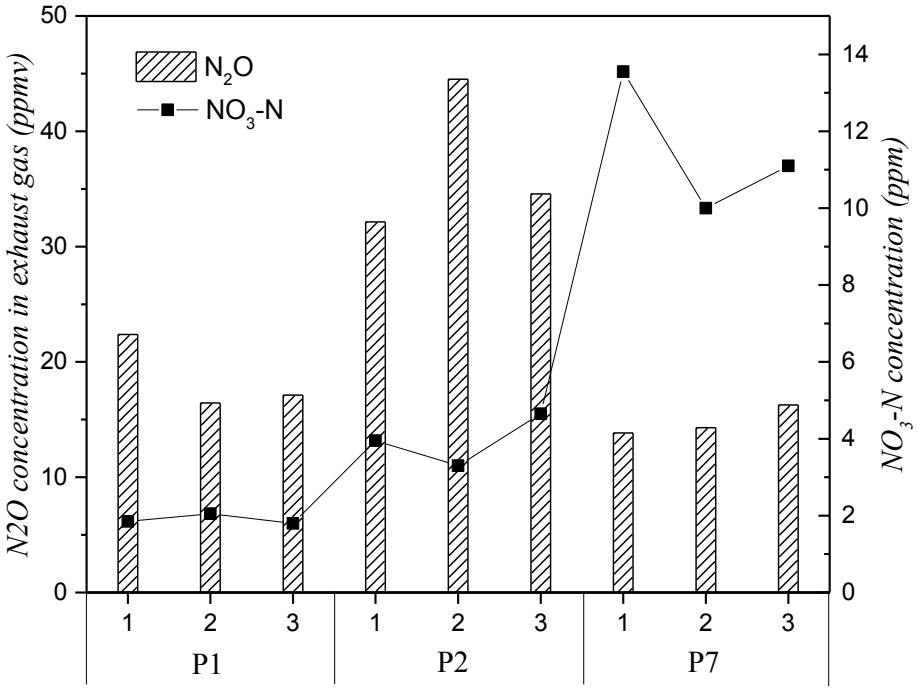


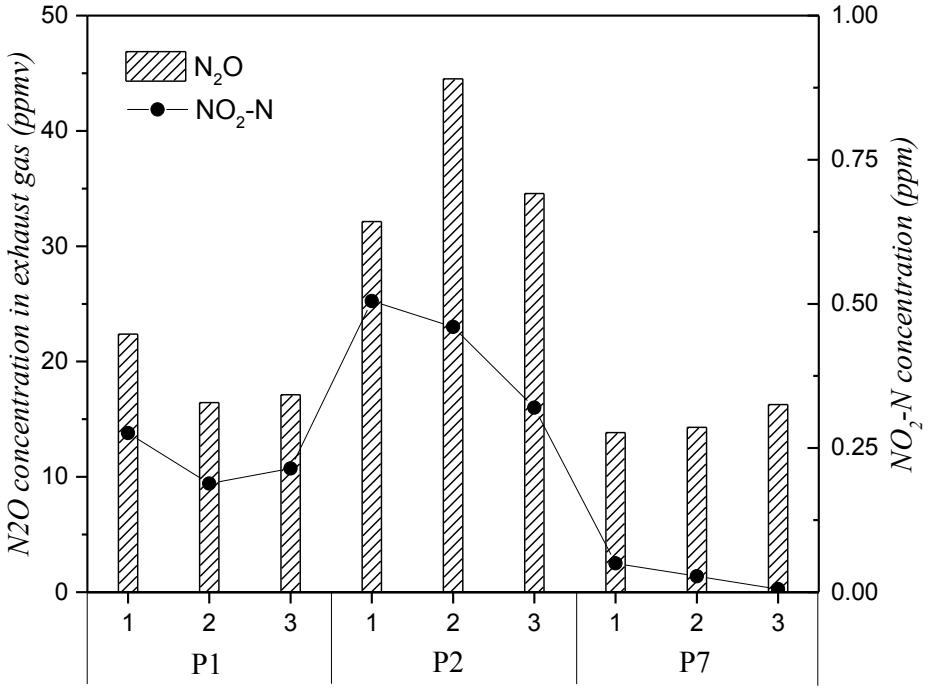
Figure 5.5. Dissolved N_2O concentrations measured at all seven points of the bioreactor.

5.5.2. Nitrate, nitrite, ammonia and DO

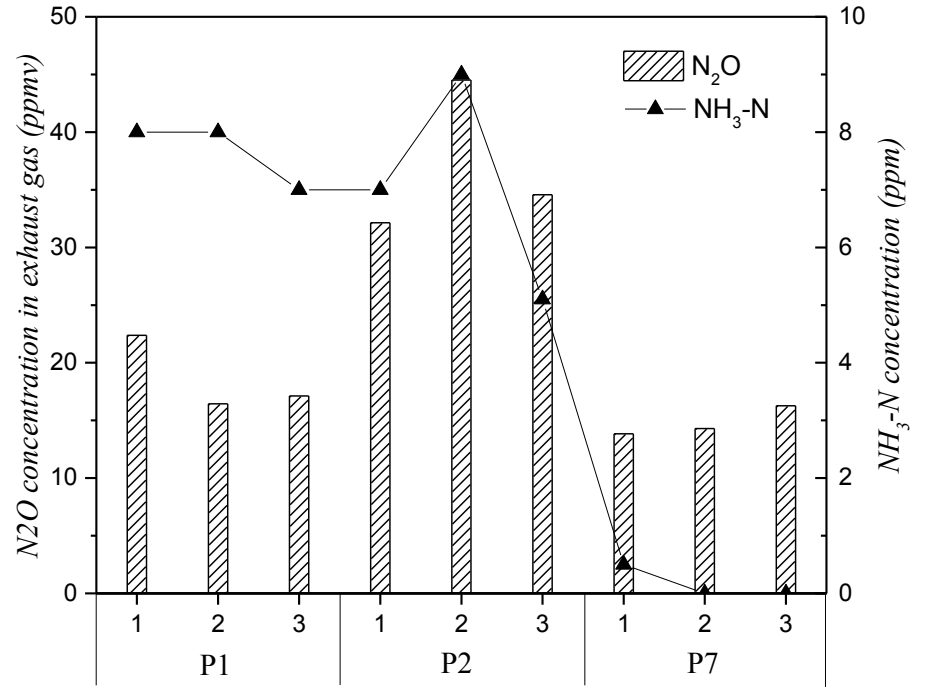
Comparison of the N_2O emission for the three monitoring points (P1, P2 and P7) and corresponding wastewater parameters are illustrated in Figure 5.6. For each point, there were three samples analyzed on three days. The corresponding concentrations of (a) nitrate, (b) nitrite, (c) ammonia and (d) DO are also shown in Figure 5.6. It can be observed from Figure 5.6 that among the four water parameters, only nitrite showed a similar trend with the N_2O emission rate.


N2O concentration in exhaust gas (ppmv)
NO3-N concentration (ppm)
N2O
NO3-N
0
10
20
30
40
50
0
2
4
6
8
10
12
14
1
2
3
1
2
3
1
2
3
P1
P2
P7

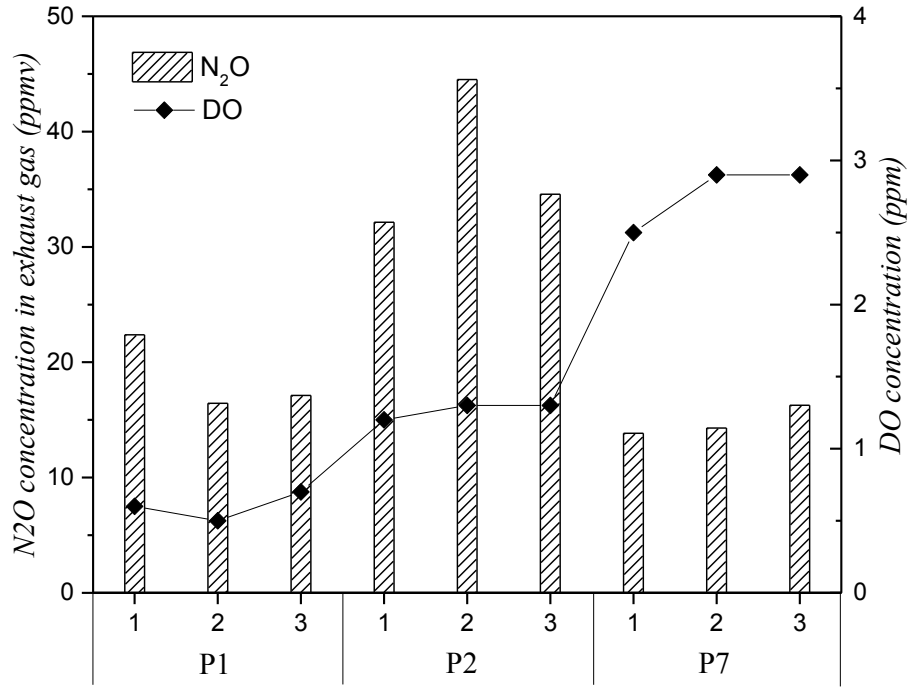
(a)


N2O concentration in exhaust gas (ppmv)
NO2-N concentration (ppm)
N2O
NO2-N
50
40
30
20
10
0
1.00
0.75
0.50
0.25
0.00
1 2 3 1 2 3 1 2 3
P1
P2
P7

(b)


N2O concentration in exhaust gas (ppmv)
NH3-N concentration (ppm)
N2O
NH3-N
50
40
30
20
10
0
10
8
6
4
2
0
1 2 3 1 2 3 1 2 3
P1
P2
P7

(c)



(d)

Figure 5.6. Gaseous N_2O emission versus (a) NO_3^-; (b) NO_2^-; (c) NH_3; (d) DO.

From correlation analysis by SPSS on all the aqueous parameters (Table 5.2), it had been found that the correlation was significant at the 0.01 level between nitrite and N_2O emission. This result is identical with previous observation in the CWRP. The corresponding Pearson Correlation Coefficient was 0.864. No significant correlations of N_2O emission with nitrate, ammonia and DO were found.

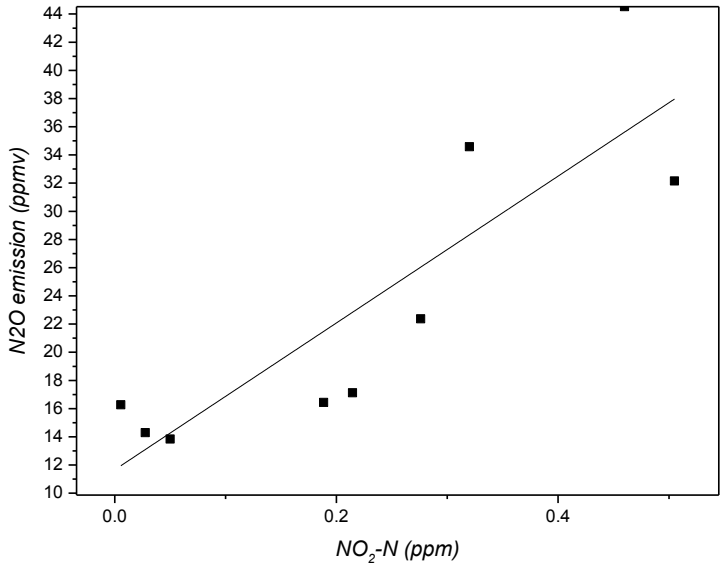
The linear relationship is illustrated in Figure 5.7, with corresponding slope and interception values displayed.

Table 5.2. Pearson correlations among N_2O emission and wastewater parameters.

		N_2Ogas	NO_2-N	NH_3-N	NO_3-N	DO
N_2Ogas	Pearson Correlation	1	.864**	.581	-.447	-.335
	Sig. (2-tailed)		.003	.101	.228	.378
	N	9	9	9	9	9
NO_2-N	Pearson Correlation	.864**	1	.809**	-.700*	-.646
	Sig. (2-tailed)	.003		.008	.036	.060
	N	9	9	9	9	9
NH_3-N	Pearson Correlation	.581	.809**	1	-.943**	-.936**
	Sig. (2-tailed)	.101	.008		.000	.000
	N	9	9	9	9	9
NO_3-N	Pearson Correlation	-.447	-.700*	-.943**	1	.939**
	Sig. (2-tailed)	.228	.036	.000		.000
	N	9	9	9	9	9
DO	Pearson Correlation	-.335	-.646	-.936**	.939**	1
	Sig. (2-tailed)	.378	.060	.000	.000	
	N	9	9	9	9	9

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).



	Value	Standard Error
Intercept	11.66162	3.26886
Slope	52.08955	11.4775

Figure 5.7. Linear correlation between N_2O emission and NO_2^-.

5.6. Monitoring at Odor Control System

For the UPWRP, off-gas was blown into the air duct of the odor control system with a positive pressure. Gas samples were taken from both the inlet and outlet of the odor control system for analysis. Gas samples collected at the inlet of the air duct represented the raw exhaust gas from the bioreactors. Gas samples collected at the outlet of the air duct represented the treated exhaust gas to be disposed to the atmosphere. Table 5.3 showed the N_2O concentrations in the gas samples.

Table 5.3. N_2O concentrations monitored at the air duct of the odor control system of the South Work of the UPWRP.

Sampling Session	*Sampling Location*	*Average N_2O concentration (mg/m^3)*
Session 1	Outlet	16.67
	Outlet	16.67
Session 2	Inlet	14.17
	Outlet	14
	Outlet	14.33
Session 3	Inlet	16.19
	Outlet	15.45

The N_2O concentration in the air duct was relatively stable during the monitoring period. It can be observed that there was little difference between the inlet and outlet N_2O concentrations. This implied that the odor treatment process, which uses activated carbon, was unable to remove N_2O in the exhaust gas. In other words, the N_2O, produced during the BNR process, present in the off-gas was completely released to the atmosphere.

There were seven parallel air ducts in the odor control facility at the South Work of the UPWRP for treating the exhaust gas. Two of the air ducts were on standby while the other five were functioning. The designed average air flow rate in a single air duct was 180 m^3/min. Therefore, the overall N_2O emission monitored from the odor control system was about 19.9±1.5 kg/d, which was slightly less than the amount estimated from online monitoring results.

The result was reasonable despite the fact that the entire bioreactor process was covered up, the headspace of the reactors was not completely isolated from the ambient air. This might result in N_2O loss from the cover gaps caused by turbulence and diffusion. However, the difference was not significant between the two results, suggesting a good exhaust gas pumping efficiency by the odor control system.

5.7. Discussion

The online monitoring at the full-scale bioreactor in the UPWRP was accomplished within three months. The N_2O emission fraction of the plug-flow BNR bioreactor was 0.168±0.026% of the influent nitrogen and 0.228±0.035% of the TN removed. Compared to the results from previous studies listed in Table 2.1, of which the N_2O emission fraction varied from 0 to 25%, the overall N_2O emission fraction of 0.168±0.026% from the South Work of the UPWRP was at a relatively low level. It has been concluded that 95.52% of the total N_2O emission from the BNR process of the UPWRP was contributed by the aerobic zones, while the anoxic zone contributed at a relatively low level. This finding strongly validated the earlier studies that majority of N_2O emission was from the aeration zones (Ahn et al., 2010; Foley et al., 2010). Nevertheless, it could not be extrapolated from this finding whether it was nitrification or denitrification that lead to more N_2O generation during the nitrogen removal process. N_2O was produced during both nitrification and denitrification, while aerobic tanks contributed to more emission due to air stripping (Ahn et al., 2010).

NO_x emission was at a comparably low level, of which over 99% monitored in the gas mixture was NO.

Even though at low concentrations, the dissolved N_2O in the anoxic zone was comparably higher than that in the aerobic zone. However, the emitted N_2O into the gaseous phase was proven to be much higher from the aerobic zone. This phenomenon was consistent with previous studies on online monitoring that N_2O generated during denitrification in the anoxic zone could accumulate in the aqueous phase. The accumulated N_2O can then be stripped out after being sent to the aerobic zone (Law et al., 2011).

In both the CWRP and UPWRP, nitrite concentration has been found to be an outstanding parameter that was positively correlated to N_2O emission, which was identical with earlier studies (Chandran, 2012; Foley et al., 2010; Kampschreur et al., 2009, 2008b; Sümer et al., 1995). The overall N_2O emission from the plug-flow reactors in the UPWRP was much lower than that in the CWRP. This can be reflected in the much lower nitrite concentration in the mixed liquor during full nitrification process.

The online monitoring could not be implemented at all necessary points due to site restriction, hence the monitoring did not include the possible spatial variation of N_2O emission. The estimation of the aerobic basin was calculated based on data from limited points, namely the beginning and the end. It was known that nitrite concentration was higher at the central part in the plug-flow reactor (P4 & P5 in Figure 5.4). Based on the correlation between nitrite and N_2O emission, it can be extrapolated that the N_2O at the central portion of the

reactor would be higher. Accordingly there would be an underestimation in the total N_2O emission.

While being blown into the odor control system, a portion of the off-gas may escape from the incompletely isolated covered tanks. Therefore, the N_2O emission monitored from the odor control system was a bit lower than the actual one. However, there was only a little difference between the monitored data from the air duct and from online monitoring, indicating a good blowing efficiency of the odor control system. The gas treatment process in the odor control system had been proven that it does not remove gaseous N_2O.

Chapter 6: Conclusions and Recommendations

6.1. Conclusions

In this study, a newly developed prototype for online monitoring of nitrogen greenhouse gas emission from WRPs was used for quantification of nitrous oxide emission baseline from full-scale BNR reactors in Singapore Water Reclamation Plants. The sampling prototype was modified from the USEPA standard surface emission isolation flux chamber and was proven to be capable to get diurnal profile of surface N_2O emission from BNR reactors through real-time monitoring.

The N_2O emission baselines of the BNR processes in both the CWRP and UPWRP were successfully obtained. In the CWRP, the N_2O emission fraction of the aerobic zone was 1.88±0.116% of the influent TKN. In the UPWRP, the N_2O emission fraction was 0.168±0.026% of the influent nitrogen. NO_x emissions in both plants were at negligible level compared to the N_2O emission. On a yearly basis, there existed over-/underestimation in the monitoring. To get more accurate results, long-term online monitoring is recommended.

Aerobic zones significantly contributed to the total N_2O emission from a BNR process. Meanwhile, N_2O emitted from anoxic zones also contributed to the total N_2O emission at a lower level. N_2O emission from BNR processes was affected by nutrient levels and constituents in the wastewater. It has been observed from both plants that nitrite concentration was positively correlated to N_2O emission especially in the aerobic zone. Nitrate concentration was also observed to have positive correlation with N_2O emission in the CWRP.

Dissolved N_2O in the wastewater was greatly affected by aeration and temperature. There was no correlation found between gaseous N_2O emission and dissolved N_2O in the wastewater.

6.2. Recommendations

6.2.1. Comprehensive Monitoring from Full-scale BNR Processes

Both grab sampling and online monitoring are reliable methods that could be able to obtain the N_2O emission baseline of a full-scale BNR process. Grab sample is a practical choice when time limitation and site restrictions exist. The limitation of grab sampling is that it is unable to retrieve the diurnal profile of the N_2O emission, which may result in overestimation or underestimation of the overall emission. The biggest advantage of online monitoring is that it is able to obtain continuous emission profile. Thus, it is possible to capture diurnal, weekly or even monthly emission profile using online monitoring. However, the conduction of online monitoring is constrained by site restrictions including accessibility of equipment, continuous power supply and environment conditions such as temperature and humidity. For both grab sampling and online monitoring, it is recommended to monitor at multiple locations to cover the spatial variations of the N_2O emission, for example, different aerobic zones of one reactor will have different emission. To cover the seasonal variation of the emission, it is necessary for both monitoring methods to be carried out in different seasons because temperature and precipitation could have great effect

on N_2O emission. Long-term monitoring is highly recommended for the purpose of obtaining a comprehensive emission profile.

In case there is restriction to access the BNR reactor, an alternative way to estimate the amount of the overall N_2O emission is to conduct monitoring at the off-gas air duct if the plant has odor control facilities that collect off-gas from all bioreactors. However, the monitoring result may not be accurate in case the reactors are not hundred percent isolated from the ambient air. Even though there might be off-gas loss from the air duct, it could be a good estimation of the overall emission.

6.2.2. Reduction of N_2O Emission from the BNR Processes in the CWRP

Since it has been concluded that N_2O emission is positively correlated with nitrite concentration during a BNR process, a straightforward forward way to reduce N_2O emission from CWRPs is to control the nitrite concentration in the process. Usually a full nitrification process could rarely have high nitrite accumulation in the aeration zone. For reactors with non-purposive partial nitrification like the BNR process in the CWRP, the process could be reformed into full nitrification by engineering methods. There might be complex factors affecting the nitrification process such as pH, temperature, microbial ecology and biological kinetics. For existing plants, two theoretical ways to control partial nitrification process to full nitrification process are to raise the DO level and increase the solids retention time. On the other hand, increased aeration rate

could result in stronger air stripping. Therefore, the optimum operating conditions are to be determined by long-term studies.

6.2.3. Further Studies on N_2O Emission from BNR Processes

This study has developed a modified SEIFC to capture off-gas from bioreactors to quantify the N_2O emission from full-scale BNR processes and has found correlation between gaseous N_2O emission and aqueous parameters. The intensive monitoring of N_2O emission from the full-scale BNR processes in both of the CWRP and UPWRP lasted for several months within a single season. The calculated baseline could only represent the emission during the certain period but not emissions in the future. Therefore, to get a better understanding of the yearly change of the emission, periodic monitoring, i.e., every six months or every year, at the same plant is recommended.

The factors affecting N_2O emission in a full-scale BNR reactor could be complex and the emission level could not be estimated from single factors. To have a better understanding of the N_2O emission for the purpose of reducing N_2O emission, it is essential to understand the leading mechanisms and influencing factors in a full-scale plant. Therefore, more comprehensive analysis of possible affecting factors should be investigated. Besides wastewater characteristics and operational conditions, environmental conditions such as temperature and partial pressure should be also taken into account.

References

Ahn, J.H., Kim, S., Park, H., Rahm, B., Pagilla, K., Chandran, K., 2010. N2O emissions from activated sludge processes, 2008-2009: results of a national monitoring survey in the United States. Environ. Sci. Technol. 44, 4505–4511. doi:10.1021/es903845y

Ahn, J.H., Kwan, T., Chandran, K., 2011. Comparison of partial and full nitrification processes applied for treating high-strength nitrogen wastewaters: Microbial ecology through nitrous oxide production. Environ. Sci. Technol. 45, 2734–2740. doi:10.1021/es103534g

Anderson, B., Bartlett, K., Frolking, S., Hayhoe, K., 2010. Methane and nitrous oxide emissions from natural sources. United States Environ. ….

Andersson, K.K., Hooper, A.B., 1983. O2 and H2O are each the source of one O in NO−2 produced from NH3 by Nitrosomonas: 15N-NMR evidence. FEBS Lett. doi:10.1016/0014-5793(83)80292-0

Benckiser, G., Eilts, R., Linn, A., Lorch, H.J., Sümer, E., Weiske, A., Wenzhöfer, F., 1996. N2O emissions from different cropping systems from aerated, nitrifying denitrifying tanks of a municipal waste water treatment plant. Biol. Fertil. Soils 23, 257–265. doi:10.1007/s003740050169

Brettar, I., Hofle, M.G., 1993. Nitrous oxide producing heterotrophic bacteria from the water column of the central Baltic: abundance and molecular identification. Mar. Ecol. Ser. 94, 253–265.

Burgess, J.E., Colliver, B.B., Stuetz, R.M., Stephenson, T., 2002. Dinitrogen oxide production by a mixed culture of nitrifying bacteria during ammonia shock loading and aeration failure. J. Ind. Microbiol. Biotechnol. 29, 309–313.

Butler, M.D., Wang, Y.Y., Cartmell, E., Stephenson, T., 2009. Nitrous oxide emissions for early warning of biological nitrification failure in activated sludge. Water Res. 43, 1265–1272. doi:10.1016/j.watres.2008.12.027

Cantera, J.J.L., Stein, L.Y., 2007. Molecular diversity of nitrite reductase genes (nirK) in nitrifying bacteria. Environ. Microbiol. 9, 765–776. doi:10.1111/j.1462-2920.2006.01198.x

Casciotti, K.L., Ward, B.B., 2005. Phylogenetic analysis of nitric oxide reductase gene homologues from aerobic ammonia-oxidizing bacteria. Fems Microbiol. Ecol. 52, 197–205.

Chandran, K., 2010. Protocol for the measurement of nitrous oxide fluxes from biological wastewater treatment plants, 1st ed, Methods in Enzymology. Elsevier Inc. doi:10.1016/B978-0-12-381294-0.00016-X

Chandran, K., 2012. Greenhouse Nitrogen Emissions from Wastewater Treatment Operation Phase I: Molecular Level Through Whole Reactor Level Characterization.

Chiu, Y.C., Chung, M.S., 2000. BNP test to evaluate the influence of C/N ratio on N2O production in biological denitrification, in: Water Science and Technology. pp. 23–27.

Czepiel, P., Crill, P., Harriss, R., 1995. Nitrous oxide emissions from municipal wastewater treatment. Environ. Sci. & Technol. 29, 2352–2356.

Daelman, M.R.J., De Baets, B., van Loosdrecht, M.C., Volcke, E.I., 2013a. Influence of sampling strategies on the estimated nitrous oxide emission from wastewater treatment plants. Water Res 47, 3120–3130.

Daelman, M.R.J., Van Voorthuizen, E.M., Van Dongen, L.G.J.M., Volcke, E.I.P., Van Loosdrecht, M.C.M., 2013b. Methane and nitrous oxide emissions from municipal wastewater treatment - Results from a long-term study. Water Sci. Technol. 67, 2350–2355.

Foley, J., de Haas, D., Yuan, Z., Lant, P., 2010. Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. Water Res. 44, 831–844. doi:10.1016/j.watres.2009.10.033

Foley, J., Yuan, Z., Keller, J., Senante, E., Chandran, K., Willis, J., Shah, S., van Loosdrecht, M., van Voorthuizen, E., 2011. N2O and CH4 emissions from wastewater collection and treatment systems, technical report.

Frijns, J., Roorda, J., Mulder, M., 2008. Op weg naar een klimaatneutrale waterketen. H_2O 10, 36-37.

Garbeva, P., Baggs, E.M., Prosser, J.I., 2007. Phylogeny of nitrite reductase (nirK) and nitric oxide reductase (norB) genes from Nitrosospira species isolated from soil. FEMS Microbiol. Lett. 266, 83–89. doi:10.1111/j.1574-6968.2006.00517.x

Garrido, J.M., Moreno, J., Méndez-Pampín, R., Lema, J.M., 1998. Nitrous oxide production under toxic conditions in a denitrifying anoxic filter. Water Res. 32, 2550–2552. doi:10.1016/S0043-1354(97)00433-8

Goreau, T.J., Kaplan, W.A., Wofsy, S.C., 1980. Production of NO2 - and N2O by nitrifying bacteria at reduced concentrations of oxygen. Appl. Environ. Microbiol.

Hanaki, K., Hong, Z., Matsuo, T., 1992. Production of nitrous oxide gas during denitrification of wastewater. Proc. 16th Bienn. Conf. Int. Assoc. Water Pollut. Res. Control - Water Qual. Int. '92 26, 1027–1036.

Hegerl, G.C., Zwiers, F.W., Braconnot, P., Gillett, N.P., Luo, Y., Orsini, J. a M., Nicholls, N., Penner, J.E., Stott, P. a, 2007. Understanding and attributing climate change, in Climate Change 2007. Clim. Chang. 2007 Phys. Sci. Basis.

Hooper, A.B., Vannelli, T., Bergmann, D.J., Arciero, D.M., 1997. Enzymology of the oxidation of ammonia to nitrite by bacteria. Antonie van Leeuwenhoek, Int. J. Gen. Mol. Microbiol. 71, 59–67.

Igarashi, N., Moriyama, H., Fujiwara, T., Fukumori, Y., Tanaka, N., 1997. The 2.8 A structure of hydroxylamine oxidoreductase from a nitrifying chemoautotrophic bacterium, Nitrosomonas europaea. Nat. Struct. Biol. 4, 276–284. doi:10.1038/nsb0497-276

IPCC, 1995. IPCC Second Assessment Report: Climate Change 1995.

IPCC, 2001. IPCC Third Assessment Report: Climate Change 2001, Working Group I: The Scientific Basis.

IPCC, 2007a. IPCC Fourth Assessment Report: Climate Change 2007, The AR4 Synthesis Report, 2.4 Attribution of climate change.

IPCC, 2007b. IPCC Fourth Assessment Report: Climate Change 2007, Working Group I "The Physical Science Basis" 2.10.2 Dir.

Joss, A., Salzgeber, D., Eugster, J., König, R., Rottermann, K., Burger, S., Fabijan, P., Leumann, S., Mohn, J., Siegrist, H.R., 2009. Full-scale nitrogen removal from digester liquid with partial nitritation and anammox in one SBR. Environ. Sci. Technol. 43, 5301–5306. doi:10.1021/es900107w

Kampschreur, M.J., Tan, N.C.G., Kleerebezem, R., Picioreanu, C., Jetten, M.S.M., Van Loosdrecht, M.C.M., 2008a. Effect of dynamic process conditions on nitrogen oxides emission from a nitrifying culture. Environ. Sci. Technol. 42, 429–435. doi:10.1021/es071667p

Kampschreur, M.J., Temmink, H., Kleerebezem, R., Jetten, M.S., van Loosdrecht, M.C., 2009. Nitrous oxide emission during wastewater treatment. Water Res 43, 4093–4103.

Kampschreur, M.J., van der Star, W.R., Wielders, H.A., Mulder, J.W., Jetten, M.S., van Loosdrecht, M.C., 2008b. Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment. Water Res 42, 812–826.

Kester, R. a, De Boer, W., Laanbroek, H.J., 1997. Production of NO and N (inf2) O by Pure Cultures of Nitrifying and Denitrifying Bacteria during Changes in Aeration. Appl. Environ. … 63, 3872–3877.

Kim, S.W., Miyahara, M., Fushinobu, S., Wakagi, T., Shoun, H., 2010. Nitrous oxide emission from nitrifying activated sludge dependent on denitrification by ammonia-oxidizing bacteria. Bioresour. Technol. 101, 3958–3963. doi:10.1016/j.biortech.2010.01.030

Kimochi, Y., Inamori, Y., Mizuochi, M., Xu, K.Q., Matsumura, M., 1998. Nitrogen removal and N2O emission in a full-scale domestic wastewater treatment plant with intermittent aeration. J. Ferment. Bioeng. 86, 202–206. doi:10.1016/S0922-338X(98)80114-1

Knowles, R., 1982. Denitrification. Microbiol. Rev. 46, 43–70.

Law, Y., Lant, P., Yuan, Z., 2011. The effect of pH on N2O production under aerobic conditions in a partial nitritation system. Water Res. 45, 5934–5944. doi:10.1016/j.watres.2011.08.055

Law, Y., Ye, L., Pan, Y., Yuan, Z., 2012. Nitrous oxide emissions from wastewater treatment processes. Philos. Trans. R. Soc. B Biol. Sci. 367, 1265–1277. doi:10.1098/rstb.2011.0317

Metcalf, E., Eddy, H., 2003. Wastewater engineering: treatment and reuse, Wastewater Engineering, Treatment, Disposal and Reuse. Techobanoglous G, Burton FL, Stensel HD (eds). Tata McGraw-Hill Publishing Company Limited, 4th edition. New Delhi, India.

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Sybil Seitzinger, van Cleemput, O., 1999. An overview of the revised 1996 IPCC guidelines for national greenhouse gas inventory methodology for nitrous oxide from agriculture. Environ. Sci. Policy. doi:10.1016/S1462-9011(99)00022-2

National Oceanic and Atmospheric Administration, Earth System Research Laboratory. 2015. The NOAA annual greenhouse gas index (AGGI). Retreived 2015 from http://www.esrl.noaa.gov/gmd/aggi/aggi.html.

Otte, S., Grobben, N.G., Robertson, L.A., Jetten, M.S., Kuenen, J.G., 1996. Nitrous oxide production by Alcaligenes faecalis under transient and dynamic aerobic and anaerobic conditions. Appl. Environ. Microbiol. 62, 2421–2426.

Poughon, L., Dussap, C.G., Gros, J.B., 2001. Energy model and metabolic flux analysis for autotrophic nitrifiers. Biotechnol. Bioeng. 72, 416–433. doi:10.1002/1097-0290(20000220)72:4<416::AID-BIT1004>3.0.CO;2-D

Ravishankara, A.R., Daniel, J.S., Portmann, R.W., 2009. Nitrous oxide (N2O): the dominant ozone-depleting substance emitted in the 21st century. Science 326, 123–125. doi:10.1126/science.1176985

Richardson, D., Felgate, H., Watmough, N., Thomson, A., Baggs, E., 2009. Mitigating release of the potent greenhouse gas N2O from the nitrogen cycle - could enzymic regulation hold the key? Trends Biotechnol. doi:10.1016/j.tibtech.2009.03.009

Rodriguez-Caballero, A., Ribera, A., Balcazar, J.L., Pijuan, M., 2013. Nitritation versus full nitrification of ammonium-rich wastewater: comparison in terms of nitrous and nitric oxides emissions. Bioresour Technol 139, 195–202.

Schalk-Otte, S., Seviour, R.J., Kuenen, J.G., Jetten, M.S.M., 2000. Nitrous oxide (N2O) production by Alcaligenes faecalis during feast and famine regimes. Water Res. 34, 2080–2088. doi:10.1016/S0043-1354(99)00374-7

Schmidt, C.E., 2008. VALIDATION OF THE MODIFIED USEPA FLUX CHAMBER TECHNOLOGY FOR ASSESSING HIGH ADVECTIVE FLOW SOURCES SUCH AS BIOFILTERS AT COMPOST SITES. 16th Annu. US Compost. Counc. Conf.

Schmidt, I., Bock, E., 1997. Anaerobic ammonia oxidation with nitrogen dioxide by Nitrosomonas eutropha. Arch. Microbiol. 167, 106–111.

Shaw, L.J., Nicol, G.W., Smith, Z., Fear, J., Prosser, J.I., Baggs, E.M., 2006. Nitrosospira spp. can produce nitrous oxide via a nitrifier denitrification pathway. Environ. Microbiol. 8, 214–222. doi:10.1111/j.1462-2920.2005.00882.x

Sommer, J., Ciplak, G., Linn, A., Sumer, E., Benckiser, G., Ottow, J.C.G., 1998. Quantification of emitted and retained N2O in a municipal waste water treatment plant with activated sludge and nitrifying-denitrifying units. Agribiol. Res. Fur Agrarbiol. Agrik. Okol. 51, 59–73.

Sümer, E., Weiske, A., Benckiser, G., Ottow, J.C.G., 1995. Influence of environmental conditions on the amount of N20 released from activated sludge in a domestic waste water treatment plant. Experientia 2, 419–422. doi:10.1007/BF01928908

Tallec, G., Garnier, J., Billen, G., Gousailles, M., 2006. Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of urban wastewater treatment plants: Effect of oxygenation level. Water Res 40, 2972–2980.

Tallec, G., Garnier, J., Billen, G., Gousailles, M., 2006. Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of

urban wastewater treatment plants: Effect of oxygenation level. Water Res. 40, 2972–2980. doi:10.1016/j.watres.2006.05.037

Thomsen, M., Lyck, E., 2005. Emission of CH4 and N2O from Wastewater Treatment Plants (6B).

Townsend-Small, A., Pataki, D.E., Tseng, L.Y., Tsai, C.Y., Rosso, D., 2011. Nitrous oxide emissions from wastewater treatment and water reclamation plants in Southern California. J. Environ. Qual. 40, 1542–1550.

Unfccc, 1998. Kyoto Protocol To the United Nations Framework Kyoto Protocol To the United Nations Framework. Rev. Eur. Community Int. Environ. Law 7, 214–217. doi:10.1111/1467-9388.00150

UNFCCC, 2014. Global Warming Potentials [WWW Document]. United Nations Framew. Conv. Clim. Chang. URL http://unfccc.int/ghg_data/items/3825.php

Wei, D., Shi, L., Zhang, G., Wang, Y., Shi, S., Wei, Q., Du, B., 2014. Comparison of nitrous oxide emissions in partial nitrifying and full nitrifying granular sludge reactors treating ammonium-rich wastewater. Bioresour. Technol. 171, 487–490. doi:10.1016/j.biortech.2014.08.071

Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Mar. Chem. doi:10.1016/0304-4203(80)90024-9

Wicht, H., 1996. A model for predicting nitrous oxide production during denitrification in activated sludge, in: Water Science and Technology. pp. 99–106. doi:10.1016/0273-1223(96)00634-8

Wicht, H., Beier, M., 1995. N2O-Emissionen aus nitrifizierenden und denitrifizierenden Kläranlagen / N2O emissions from nitrifying and denitrifying sewage treatment plants. Korrespondenz Abwasser 42(3), 404–406,411–413.

Yang, Q., Liu, X., Peng, C., Wang, S., Sun, H., Peng, Y., 2009. N2O production during nitrogen removal via nitrite from domestic wastewater: Main sources and control method. Environ. Sci. Technol. 43, 9400–9406. doi:10.1021/es9019113

Ye, L., Ni, B.J., Law, Y., Byers, C., Yuan, Z., 2014. A novel methodology to quantify nitrous oxide emissions from full-scale wastewater treatment systems with surface aerators. Water Res 48, 257–268.

Yu, R., Kampschreur, M.J., Van Loosdrecht, M.C.M., Chandran, K., 2010. Mechanisms and specific directionality of autotrophic nitrous oxide and nitric oxide generation during transient anoxia. Environ. Sci. Technol. 44, 1313–1319. doi:10.1021/es902794a

Zeng, R.J., Lemaire, R., Yuan, Z., Keller, J., 2003. Simultaneous nitrification, denitrification, and phosphorus removal in a lab-scale sequencing batch reactor. Biotechnol. Bioeng. 84, 170–178. doi:10.1002/bit.10744